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BULLETIN OF THE
CHEMICAL SOCIETY OF JAPAN

The Absorption Spectra of Nitrocellulose.

By Kôiti MASAKI.

(Received October 30th, 1936.)

On account of the lack of a suitable solvent it has been hard to obtain the ultraviolet absorption spectra of nitrocellulose. B. Rassow and W. Aehnelt[1] used ether-alcohol as the solvent, but the maximum concentration was only 2 g. in 1000 c.c., namely, 7.94×10^{-3} mol as regards the dinitroglucose unit. Therefore, the characteristic absorption of nitrocellulose remains yet undiscovered, and the linear end-absorption has not been interpreted. Considered from the author's previous consideration, the selective absorption might be observed at a higher concentration or with a thicker layer. A good result has been obtained by using clear films of nitrocellulose prepared with a suitable solvent, instead of solutions, which appeared extremely difficultly to be raised to a concentration higher than Rassow's case. By the film method it was easy to obtain two absorptions (3300–2500 Å and below 2500 Å) which may be reasonably attributed to the nitro-groups as the case of nitroglycerine.[2]

Experimental. The preparation of good films depends chiefly on the selection of the solvent and on the technique of evaporation. Since the solvent remains in films in amounts of a few percent, it must not absorb above 2200 Å. The author used ether-alcohol (80 g. ether and 40 g. alcohol for 2 g. of nitrocellulose) or acetone as the solvent. The mixture of nitrocellulose and the solvent was frequently stirred or shaken so as to bring the suspended nitrocellulose into solution. After standing overnight, 10 c.c. of the filtered solution was spread over the surface of mercury. The liquid film was gradually evaporated to a clear solid film by evacuation in the course of a few days. Different numbers of films of about 1/100 mm. thickness were placed between two quartz plates. From the weight, the area, and the density (1.65), of the films, the thickness was computed. The experiments were carried out in the same way as in the case of nitroglycerine except that exposure time was 7 minutes. In the accompanying figure the logarithm of relative thickness is plotted against the wave number. From the figure, it is established that there are two absorptions.

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(1) *Cellulosechem.*, **10** (1929), 163.
(2) This Bulletin, **11** (1936), 712.

Table 1 (Curve 1). Films prepared with acetone. Ilford Special Rapid Panchromatic Plates.

Thickness d (mm.)	log d	log of relative thickness* log D	Wave length (Å)	Wave number (mm.$^{-1}$)
0.246	$\bar{1}$.389	3.506	3185	3139
0.223	$\bar{1}$.348	3.465	3125	3199
0.200	$\bar{1}$.301	3.418	3075	3251
0.161	$\bar{1}$.207	3.324	3000	3332
0.104	$\bar{1}$.017	3.134	2869	3482
0.060	$\bar{2}$.778	2.895	2745	3642
0.051	$\bar{2}$.708	2.825	2647	3777
0.046	$\bar{2}$.663	2.780	2603	3841
0.023	$\bar{2}$.362	2.479	2460	4070

Table 2 (Curve 2). Films prepared with ether-alcohol. Ilford Special Rapid Panchromatic Plates.

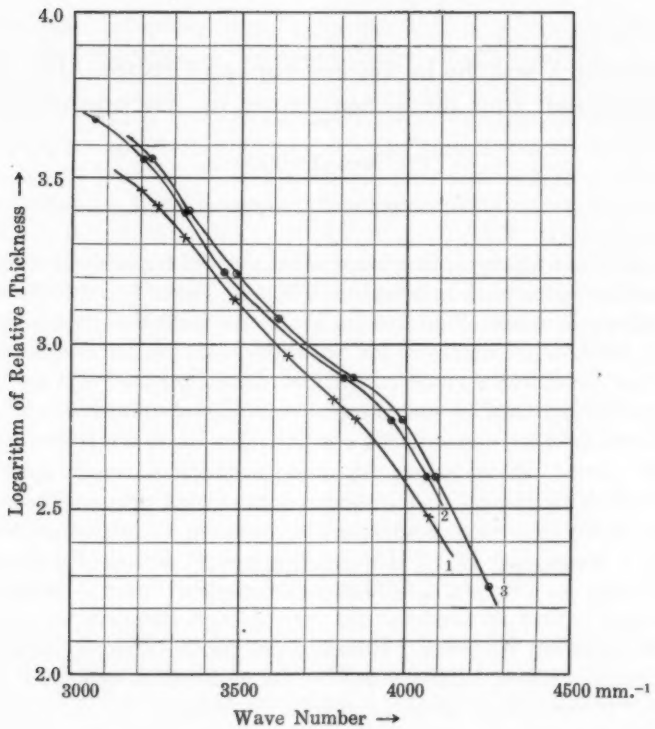
0.549	$\bar{1}$.740	3.857	—	—
0.450	$\bar{1}$.653	3.770	3754	2663
0.359	$\bar{1}$.555	3.672	3265	3062
0.273	$\bar{1}$.436	3.553	3101	3224
0.130	$\bar{1}$.279	3.396	2994	3339
0.124	$\bar{1}$.093	3.210	2891	3458
0.060	$\bar{2}$.778	2.895	2630	3816
0.030	$\bar{2}$.477	2.594	2459	4066

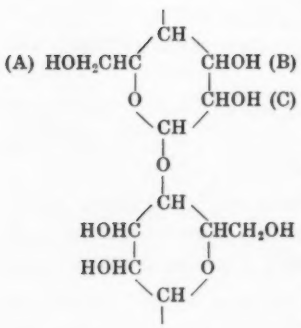
Table 3 (Curve 3). Films prepared with ether-alcohol. Ilford Schumann Plates.

0.273	$\bar{1}$.436	3.553	3089	3236
0.190	$\bar{1}$.279	3.396	2992	3341
0.124	$\bar{1}$.093	3.210	2867	3487
0.090	$\bar{2}$.954	3.072	2765	3616
0.060	$\bar{2}$.778	2.895	2600	3845
0.045	$\bar{2}$.653	2.771	2512	3980
0.030	$\bar{2}$.477	2.594	2444	4090
0.014	$\bar{2}$.146	2.263	2348	4258

* The equivalent thickness of N/2000 of the dinitroglucose unit, calculated from Beer's law. ($\log D = \log d + 4.117$)

Discussion. Considered from the molecular structure it is obvious that these absorptions of nitrocellulose must be attributed to the nitro-groups. When the molecular weight of nitroglucose unit in nitrocellulose divided by the number of nitro-groups is taken as one gram mol, the absorption intensity of nitrocellulose ($\log \varepsilon = 1.1$)[2] is very nearly coincident with the cases of the other nitro-esters and nitro-compounds. If the hydroxyl-groups in the glucose structure considered as the unit of cellulose are marked A, B, and C, as shown in the formula, the combination of AB or of AC may be the most possible for the positions of two nitro-groups in the case of nitrocellulose containing 11%





nitrogen, because a structure with a considerable distance between the two nitro-groups is probably more stable on account of a small interaction between them. It is, therefore, reasonable that the experiments are in excellent agreement with the values calculated for the absorption due to nitro-groups.

In the case of the nitrocellulose of a higher nitrogen content, the absorption seems to remain unchanged as in the case of nitroglycerine, because each of nitro-groups combines indirectly with a different carbon atom by a bridge of an oxygen atom and moreover may also maintain mutually a considerable distance in order to minimize the interaction.

The general discussion will be given later.

Synthetische Versuche in der Selenophen-Gruppe. III. β-Nitroselenophen und die Orientierung im Selenophen-Kern.

Von Sumio UMEZAWA.

(Eingegangen am 14, November 1936.)

Wenn in ein Monosubstitutionsprodukt des Selenophens ein zweiter Substituent eingeführt wird, so hängt es, wie beim Furan[1] und Thiophen[2], von der Konkurrenz zweier Faktoren ab, in welche Stelle der zweite Substituent dirigiert wird, d. h. einmal von der Natur des vorhandenen Substituenten, die auch in der Benzolreihe vorherrschend ist, dann aber auch von der grösseren Reaktionsfähigkeit der α- gegenüber den β-Wasserstoffatomen, mit anderen Worten von der nach den α-Stellen dirigierenden Kraft des Hetero-atoms.

Auf Grund dieses Satzes ist man imstande zu erschliessen, welche Isomeren sich als Haupt- und Nebenprodukte bilden müssen, wenn ein Substituent in ein mit einem solchen erster Ordnung substituiertes Selenophen eintritt. Wenn also ein 2-Halogenselenophen[3] weiter halogeniert oder nitriert wird, so entsteht 2,5-Dihalogenselenophen[3] oder 2-Halogen-5-nitroselenophen[4]; denn die Einflüsse des vorhandenen Halogen- und Selen-atoms liegen in derselben Richtung. Ebenso kann das 2-Halogen-3,5-dinitroselenophen[4] beim weiteren Nitrieren des 2-Halogen-5-nitroselenophens dargestellt werden. In demselben Sinne kann man die Bildung der 3,5-substituierten Selenophene eindeutig erschliessen, wenn an einer β-Stelle mit einem Substituenten zweiter Ordnung substituierte Selenophene weiter substituiert werden. Bei der weiteren Nitrierung des 3-Nitroselenophens entsteht also das 3,5-Dinitroselenophen (III) (siehe später).

Was aber die Orientierung des zweiten Substituenten betrifft, welcher in ein an einer α-Stelle mit einem Substituenten zweiter Ordnung besetztes Selenophen eingeführt ist, so muss man es experimentell nachweisen.

Ich habe mich deshalb mit Selenophen-2-sulfochlorid[4] und ihren Nitroprodukten weiter beschäftigt, einerseits um über die Substitutionsregeln in der Selenophenreihe klarer zu sehen, andererseits um die Konstitutionsbeweise klar zu stellen.

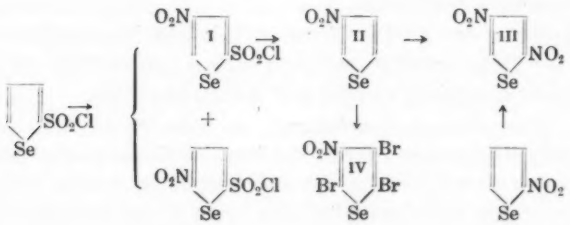
(1) H. Gilman und G. F. Wright, *Chem. Rev.*, **11** (1932), 323.

(2) W. Steinkopf und T. Höpner, *Ann.*, **501** (1933), 180; I. J. Rinks, *Rec. trav. chim.*, **53** (1934), 643.

(3) H. Suginome und S. Umezawa, dieses Bulletin, **11** (1936), 160.

(4) S. Umezawa, II. Mitteilung, dieses Bulletin, **11** (1936), 775.

Nitriert man bei tiefer Temperatur das Selenophen-2-sulfochlorid mit rauchender Salpetersäure, so entstehen Nitrosulfochloride, die aus zwei Ortsisomeren bestehen, von denen ich nur den höher schmelzenden einheitlich trennen konnte. Wenn man dann das letztere, 3-Nitroselenophen-5-sulfochlorid vom Schmelzp. 71–73.5° (I) nach der Spaltungsmethode, bei der Steinkopf und Höpner[2] in der Thiophenreihe schönen Erfolg hatten, in starker Schwefelsäurelösung bei 130–140° mit überhitzem Wasserdampf behandelt, so entsteht das β-Nitroselenophen vom Schmelzp. 77–78.5° (II) durch Abspaltung der α-Sulfonsäuregruppe. Bemerkenswert ist, dass, trotz der bisher bekannten Unbeständigkeit des Selenophenkerns gegenüber thermischer Behandlung, diese Reaktion sehr glatt verläuft und die Ausbeute 79 Proz. beträgt.



Beim Behandeln mit rauchender Salpetersäure lässt das β-Nitroselenophen sich zum 3,5-Dinitroselenophen nitrieren, welches mit dem bei weiterer Nitrierung aus α-Nitroselenophen entstandenen Dinitroderivat identisch ist.

Auf Grund der oben beschriebenen Tatsachen ist man imstande, für Substituenten zweiter Ordnung folgende Substitutionsregel beim Selenophen anzugeben: Wenn in einem an 2-Stelle besetzten Selenophen ein zweiter Substituent eingeführt wird, so tritt der letztere überwiegend in die 4-Stelle ein. Dabei entsteht keine oder nur in sehr geringer Menge eine 2,5-Verbindung. Infolgedessen ist durchaus wahrscheinlich, dass in der Selenophendisulfonsäure[4], die durch direkte Sulfonierung aus Selenophen erhalten ist, die Sulfonsäuregruppen die 2- und 4-Stellen einnehmen.

Es scheint hier von Interesse, die Orientierungseinflüsse der Heteroatome in Furan, Thiophen und Selenophen zu vergleichen. Nach Gilman und Wright[1] führt die direkte Kernsubstitution eines Mono-α-derivats des Furans zur Bildung eines α,α-Derivats, anscheinend unter Ausschluss eines α,β-Derivats. In Bezug auf die Substitutionsregeln beim Thiophen haben Steinkopf und Höpner[2] für Substituenten zweiter Ordnung geschlossen, dass bei besetzter 2-Stelle ein neuer Substituent in 4- und 5-Stelle eintritt, wobei 2,4-Verbindung meist an Menge überwiegt. Beim Selenophen tritt, wie schon erwähnt, der zweite Substituent hauptsächlich in die 4-Stelle ein. Dabei

kann man die 2,5-Verbindung nicht oder nur in sehr geringer Menge finden. Besonders entsteht kein 2,5-Dinitroselenophen beim Nitrieren von 2-Nitroselenophen. Es ist also bemerkenswert, dass eine Neigung über die Grösse der Orientierungseinflüsse von Hetero-atomen: Furan $\gg$ Thiophen $>$ Selenophen, in Übereinstimmung mit periodischer Beziehung, beobachtet wird[6].

Das β-Nitroselenophen ist der einzige β-substituierte Selenophenkörper, der weitaus beständiger als das α-Nitroselenophen ist und sich am Lichte nicht färbt. Mit Alkohol und Alkali zeigt es keine Farbenreaktion wie das α-Nitroselenophen. Daraus folgt, dass diese Farbenreaktion nicht von der Stelle der Nitrogruppe, sondern von der Zahl abhängt. Das β-Nitroselenophen lässt sich zum 2,3,5-Tribrom-4-nitroselenophen vom Schmelzp. 100.5–102° (IV) erschöpfend bromieren, beim α-Nitroselenophen aber gelang es mir infolge seiner Unbeständigkeit nicht.

Beim Reduzieren der 2,4-Disulfonsäure mit Natriumamalgam—eine von Steinkopf[5] in der Thiophenreihe ausgeführte Reaktion—wurde die α-ständige SO_3H-Gruppe nicht eliminiert, es fand nur Zersetzung statt.

Was das α-Nitroselenophen anbelangt, so habe ich schon in der zweiten Mitteilung[4] mitgeteilt, dass durch direkte Nitrierung des Selenophens Rohnitroselenophen vom Schmelzp. 38–42° gewonnen wurde. Bei der Behandlung des letzteren mit überschüssigem Brom wurde das 2,3,5-Tribrom-4-nitroselenophen (IV) isoliert. Infolgedessen zeigt es sich, dass wie beim Thiophen[2] der erste Substituent zweiter Ordnung nicht nur überwiegend in einer α-Stelle, sondern auch in geringer Menge in einer β-Stelle zu finden ist.

Es sei mir an dieser Stelle erlaubt, Herrn Prof. H. Suginome für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank auszusprechen. Gleichzeitig bin ich für Unterstützung der Kaiserlichen Akademie zu Dank verpflichtet.

Beschreibung der Versuche.

4-Nitroselenophen-2-sulfochlorid (I). 6 g. Selenophen-2-sulfochlorid werden in 20 c.c. rauchender Salpetersäure unter Umschütteln im Eiswasser nach und nach eingetragen. Die klare Reaktionslösung wird bei Zimmertemperatur etwa 20 Minuten stehen gelassen und dann in Eiswasser gegossen, wobei das Rohprodukt zu einem halbfesten Zustande erstarrt. Abgesaugt, mit Wasser gewaschen und getrocknet. Ausbeute 6.6 g. Schmp. 35–59°. Vor dem Umkrystallisieren wurden es analysiert. (Gef.: N, 5.25. Ber. für $C_4H_2O_4NClSSe$: N, 5.10%.) Es wurde dabei klar, dass in dieser Reaktion das 4-Nitroselenophen-2-sulfochlorid mit einem Ortsisomer, 5-Nitroselenophen-2-sulfochlorid beigemengt entsteht.

(5) W. Steinkopf, H. Jacob und H. Penz, *Ann.*, **512** (1934), 149.
(6) Siehe auch Suter, McKenzie und Maxwell, *J. Am. Chem. Soc.*, **58** (1936), 717.

3 g. des Präparats wurden aus Schwefelkohlenstoff viermal umkrystallisiert und nochmals analysiert. Prächtige, schwach-gelbe, säulenförmige Kryställchen. Schmp. 71–73.5°. Ausbeute 0.6 g. (Gef.: C, 17.45; H. 0.98; N, 5.19. Ber. für $C_4H_2O_4NClSSe$: C, 17.49; H, 0.73; N, 5.10%.)

Das 4-Nitroselenophen-2-sulfochlorid ist schwer löslich sogar auf dem Siedepunkte in Petroläther (40–60°), wie in Tetrachlorkohlenstoff in der Kälte. Am Lichte ist es ganz beständig und lässt sich im Exsikkator über Chlorcalzium ohne Zersetzung aufbewahren.

β-Nitroselenophen (II). (Konstitutionsermittlung des 4-Nitroselenophen-2-sulfochlorids). 5 g. 4-Nitroselenophen-2-sulfochlorid werden mit 25 c.c. Wasser durch Kochen unter Rückfluss hydrolysiert, was etwa eine Stunde in Anspruch nimmt. Die Lösung der freien 4-Nitroselenophen-2-sulfonsäure wird mit einer Mischung von 35 c.c. konzentrierter Schwefelsäure und 20 c.c. Wasser versetzt, zum Sieden erhitzt, dann mit überhitzem Wasserdampf destilliert. Die Reaktionslösung färbt sich allmählich dunkelbraun und bei 130–140° (in der siedenden Flüssigkeit) scheidet sich allmählich eine grosse Menge von schönen, farblosen Nädelchen im Kühler aus. Diese Spaltung durch überhitzen Wasserdampf nimmt etwa eine Stunde in Anspruch. Man saugt diese Kryställchen ab, wäscht sie mit Wasser und trocknet sie über Chlorcalzium. Schmp. 74–78°. Ausbeute 2.5 g., 79% der Theorie. Umkrystallisiert aus Alkohol. Farblose, aufgeschichtete Täfelchen. Schmp. 77–78.5°. (Gef.: N, 8.01; Se, 45.06. Ber. für $C_4H_3O_2NSe$: N, 7.95, Se, 44.89%.)

Krystallisiert man aus Petroläther (40–60°) um, so scheiden sich Nädelchen aus. β-Nitroselenophen färbt sich nicht am Lichte und ist im allgemeinen weitaus beständiger als α-Nitroselenophen. Mit Isatin und Schwefelsäure zeigt es keine Indopheninreaktion. Wird es mit wässerigen Alkalien gekocht, die es in der Kälte nicht lösen, so löst es sich mit braunroter Färbung auf. Mit Methanol und Kalilauge zeigt es keine Färbung.

2,4-Dinitroselenophen (III) aus 3-Nitroselenophen. 0.7 g. 3-Nitroselenophen werden in 2 c.c. rauchender Salpetersäure unter Umschütteln im Kältegemisch portionsweise eingetragen, wobei eine heftige Reaktion eintritt. Man lässt das Reaktionsgemisch sich auf Zimmertemperatur erwärmen und giesst es dann in Eiswasser ein. Bei richtiger Nitrierung scheiden sich dabei schwach-gelbe Nädelchen aus. Ausbeute 0.5 g. Schmp. 58–68°. Umkrystallisiert 4-malig aus Ligroin. Schmp. 76–78°. (Gef.: N, 12.83. Ber. für $C_4H_2O_4N_2Se$: N, 12.67%.)

Mischschmelzpunkt mit dem Präparate, das durch weitere Nitrierung aus α-Nitroselenophen erhalten wurde, zeigte keine Depression.

Dinitroselenophen verbindet sich wie Dinitrobenzol oder Dinitrothiophen mit aromatischen Kohlenwasserstoffen. Lässt man eine Lösung molekularer Mengen von Naphthalin und Dinitroselenophen in Benzol langsam verdunsten, so scheidet sich ein in schönen, gelben Nadeln krystallisierter Körper aus. Schmp. 50–53°. Er wurde in kaltem Alkohol gelöst und mit Wasser ausgefällt. Der Körper konnte unter Zusatz von Naphthalin aus Alkohol ohne Zersetzung umkrystallisiert werden und wurde in einen mit Chlorcalzium und Naphthalin beschickten Exsikkator gebracht. Schmp. 53–55°. (Gef.: N, 8.20. Ber. für $C_{14}H_{10}O_4N_2Se$: 8.0-%.) Mit Methanol und Kalilauge zeigt sich sofort schöne Rotfärbung.

2,3,5-Tribrom-4-nitroselenophen (IV). β-Nitroselenophen wird ohne Lösungsmittel mit überschüssigem Brom unter Umschütteln in Eiswasser nach und nach versetzt, wobei sich sehr heftig Bromwasserstoff entwickelt. Lässt man das Reaktionsgemisch unter Ausschluss von Feuchtigkeit einige Tage stehen, so scheidet es gelbe, säulenförmige Krystalle aus. Nach Abpressen auf die Tonplatte werden sie in Schwefelkohlenstoff

aufgelöst, mit sehr verdünntem Natriumcarbonat gewaschen, über Glaubersalz getrocknet und im Vakuum eingedunstet. Ausbeute ist fast quantitativ. Umkrystallisiert aus Alkohol. Schwach-gelbe Fadenbüschel. Schmp. 100.5-102°. (Gef.: N, 3.47; Br, 58.24. Ber. für $C_4O_2NBr_3Se$: N, 3.39; Br, 58.08%.)

Dies erwies sich im Lichte beständig und zeigte keine Farbenreaktion mit Methanol und Alkali.

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Electrolytic Reduction of Maleimide and Pyrroline.

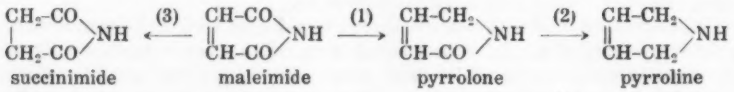
By Buhei SAKURAI.

(Received November 16th, 1936.)

In his recent researches on the electrolytic reduction of succinimide[1] and its derivatives, the present writer observed the remarkable reducing power of zinc amalgam which, when used as the cathode in a strong sulphuric acid solution, could well reduce both carbonyl groups into methylene.

In the electrolysis of pyrrol[2], however, conjugate double bonds were found not to be reduced by zinc amalgam, while the same reduction could easily be brought about by an addition of nickel. With the object of confirming whether such different behaviours of carbonyls and unsaturated carbon atoms towards the cathode are also observable in the radicals contained in a molecule, the electrolytic reduction of maleimide has been attempted.

If the above holds good, maleimide should be reduced in either one of the following ways according to the kind of cathode:



That is to say, if zinc amalgam is used as cathode, pyrroline will be obtained according to (1) and (2) and if reduced nickel is used instead, succinimide must be produced according to (3).

As the result of the experiments it was found that the reaction (3) took place quite smoothly, proceeding quantitatively at lead or copper cathode in dilute sulphuric acid solution, in which reduced nickel was suspended. With

(1) This Bulletin, **10** (1935), 311; **11** (1936), 41.
(2) This Bulletin, **11** (1936), 374.

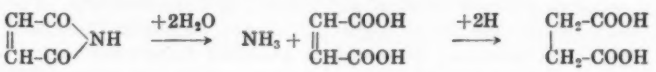
zinc amalgam cathode, however, no such reaction could be observed, the material having been decomposed into succinic acid and ammonia. For the problem how succinic acid was produced in the above electrolysis two solutions are conceivable:

(1) First maleimide is reduced to succinimide and then decomposed into succinic acid and ammonia in alkaline electrolyte.

(2) Maleimide is first decomposed into maleic acid and ammonia and maleic acid thus produced is then reduced to succinic acid.

If solution (1) be right, pyrrolidone and pyrrolidine must have been produced from succinimide according to the result previously obtained by the present writer. This is, however, contrary to the facts.

Thus solution (2) may be regarded as the more probable, that is, may be taken to occur according to the following scheme:



As the decomposition was considered to be dependent upon the concentration of sulphuric acid, experiments were repeated with 10% as well as with 30% sulphuric acid. But in no case reduction of carbonyl groups was attained.

Experimental.

Maleimide[3] was prepared by oxidising pyrrol with potassium bichromate and sulphuric acid, and obtained as sublimable brown crystals melting at 93°.

Pyrroline[4] was prepared by reducing pyrrol with zinc dust and hydrochloric acid. It was a colourless liquid with ammonia smell, boiling at 90°.

Nickel catalyser was prepared from nickel hydroxide precipitated by carefully adding a sodium hydroxide solution to nickel sulphate solution, which was first ignited and then reduced at a temperature between 320° and 330° in pure hydrogen gas.

Zinc amalgam electrode was the same that was used in the electrolysis of succinimide.

I. **Reduction of Maleimide with Reduced Nickel.** The electrolysis was undertaken under the conditions as follows: Cathode: lead tube (50 sq. cm.). Catholyte: 100 c.c. of 10% sulphuric acid and 2 g. of maleimide and 0.5 g. of reduced nickel. Anode: lead plate. Anolyte: 10% sulphuric acid. Current density: 12 amp per 100 sq. cm. Current quantity: 38.0 F per mol. Temperature: 28°.

The imide dissolved gradually in the catholyte giving a yellow solution. From time to time the nickel catalyser in the form of finest dust was added to the catholyte. The catholyte and anolyte were separated by a cylindrical vessel of biscuit, and through the cathode tube a rapid current of water was made to pass. Thus the apparatus was well cooled with water from inside and outside and the cathodic solution was stirred vigorously throughout the electrolysis. After 3.5 hours' electrolysis, the catalyser was filtered off

(3) G. Plaucher and F. Cattadori, *Atti. accad. Lincei*, (5), **13** (1904), 489.
(4) Knorr, *Ber.* **34** (1907), 3497.

from the cathodic solution. Extracting the filtrate with ether several times 1.8 g. of colourless amorphous crystals were obtained. Recrystallized from alcohol, the substance melted at 125° alone and in admixture with succinimide. Thus, the reduction product was inferred to be succinimide.

The green mother liquid was made alkaline with caustic soda, and extracted with ether. But no basic substance was obtained. This experiment shows, therefore, that succinimide was the only reduction product in the electrolysis. With copper electrode succinimide was also obtained with a yield of 80%.

II. **Reduction of Maleimide with Zinc Amalgam.** The conditions of the electrolysis were as follows: Cathode: zinc amalgam (15.8 sq. cm.). Cathodic solution: mixture of 100 c.c. of 50% sulphuric acid, 10 c.c. of alcohol, and 2 g. of maleimide. Anode: lead plate. Anodic solution: 50% sulphuric acid solution. Current density: 113.5 amp per 100 sq. cm. Current quantity: 195.8 F per mol. Temperature: 30°.

During the electrolysis, the solution was prevented from foaming by adding a small portion of alcohol, and to prevent the rise of temperature a spiral lead tube, through which cold water was rapidly running, was inserted into the catholyte. The apparatus was kept cool in water, and the catholyte was stirred vigorously throughout the electrolysis. The yellow colour of the catholyte gradually faded away as the electrolysis went on. After 6 hours the electrolysis was stopped, and the colourless cathodic solution was extracted with ether. On evaporating ether about 1.2 g. of colourless substance was obtained. When recrystallized from alcohol, this substance became prismatic crystals, which melted at 183° alone and in admixture with succinic acid. The substance, therefore, undoubtedly was succinic acid. The mother liquer, when made alkaline with a sodium hydroxide solution, emitted a distinct smell of ammonia. It was therefore subjected to steam distillation, and the distillate was acidified with hydrochloric acid, and evaporated to dryness, whereupon a colourless crystalline salt weighing about one gram was produced. The gold double salt of it did not melt at a temperature higher than 250°. Found: Au, 54.55. Calculated for $NH_4Cl \cdot AuCl_3$: Au, 55.18%. This shows that the substance was nothing but ammonium chloride, containing neither pyrrolidone nor pyrrolidine. Two more electrolyses were repeated with 10 and with 30% sulphuric acid with different results.

III. **Reduction of Maleic Acid.** As a subsidiary means of finding the cause of the production of succinic acid in the preceding experiment, maleic acid was electrolysed under the same conditions. From 2 g. of maleic acid, 1.8 g. of prismatic crystals were produced in 4 hours' electrolysis (current quantity: 130.3 F per mol). The crystals melted at 183°, the melting point of succinic acid. The yield was 83% of the theoretical.

IV. **Reduction of Pyrroline.** The electrolysis was carried out under the following conditions: Cathode: lead tube of 50 sq. cm. Cathodic solution: 2 g. of pyrroline dissolved in 100 c.c. of 10% sulphuric acid to which about 0.5 g. of reduced nickel was added from time to time. Anode: lead plate. Anodic solution: 10% sulphuric acid solution. Current density: 7 amp. per 100 sq. cm. Current quantity: 10.3 F per mol. Temperature: 29°. The electrolysis was conducted in the same manner as in I.

When the electrolysis was over, the greenish cathodic solution was taken out and made alkaline with a sodium hydroxide solution, when a strong ammonia-like smell was evolved. The solution was then subjected to steam distillation, and the distillate was evaporated after having been acidified with hydrochloric acid. Colourless needles weighing 1.5 g. were obtained. The auric double salt was produced as yellow needles,

melting at 203° with partial decomposition. Found: Au, 47.89. Calculated for $C_4H_9N \cdot HCl \cdot AuCl_3$: Au, 47.95%. It is beyond doubt that the substance was the gold salt of pyrrolidine.

The writer expresses his heartfelt thanks to Dr. Motooki Matsui, President of the Kyoto Imperial University, at whose suggestion the present work was carried out.

Osaka Women's College, Osaka.

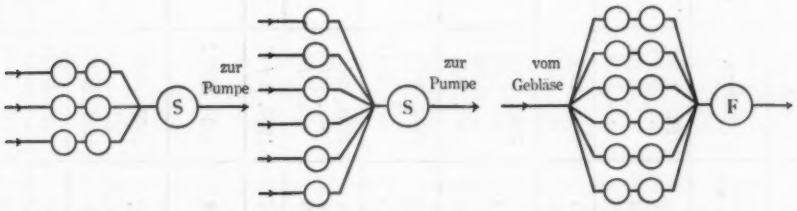
Über den Gehalt der atmosphärischen Feuchtigkeit an schwerem Wasser.

Von Kenzo OKABE und Toshizo TITANI.

(Eingegangen am 24. November 1936.)

Wir haben das spezifische Gewicht bzw. den Gehalt des durch vollständige Kondensation der atmosphärischen Feuchtigkeit unter verschiedenen Bedingungen gewonnenen Wassers an schwerem Wasser festgestellt und dieses Feuchtigkeitswasser hinsichtlich dieser Eigenschaften mit gewöhnlichem Wasser verglichen. Die Messergebnisse sind zusammen mit den Bedingungen bei der Sammlung der Proben in der beiliegenden Tabelle wiedergegeben.

Sammlung des Feuchtigkeitswassers. Bei den Versuchen von Nr. 1 bis 16 wurde die ausserhalb des Laboratoriums aufgenommene atmosphärische Luft mittels einer Wasserstrahlpumpe in mit Kohlensäureschnee-Petroleumäther-Gemisch abgekühlte leere Waschflaschen eingesaugt. Dazu wurden sechs Waschflaschen von je 15 cm. Höhe und 3 cm. l. W. benutzt, die bei den Versuchen von Nr. 1 bis 13, wie Schema Abb. a zeigt, in drei Reihen von je zwei nebeneinander angeordnet wurden. Dagegen wurden bei den Versuchen Nr. 14 bis 16 alle sechs Flaschen in einer Reihe nebeneinander gestellt (vgl. Abb. b).



a. Nr. 1 bis 13 b. Nr. 14 bis 16 c. Nr. 17 bis 22

Abb. Die Anordnung der Flasche zur Sammlung des Feuchtigkeitswassers.

Tabelle

1	2	3	4	5	6	7	8	9
Versuchsnr.	Datum	Temp. °C.	relative Feuchtigkeit in %	Barometerstand in mm. Hg	Wetter	Versuchsdauer in Stdn.	Menge des gesammelten Wassers in g.	ΔS gegen Osaka-Leitungswasser in γ
1	1935, 20/IX	23.5	64	763.5	leichter Regenfall	5.0	ca. 50	−6.8
2	,, , 21/IX	23.0	77	762	Regenwetter	4.5		
3	,, , 23/IX	22.5	77	758	,,	5.5		
4	,, , 11/X	21.0	73	761	,,	5.5		
5	1935, 25/IX	25.5	72	748	trübes Wetter	6.0	ca. 50	−4.8
6	,, , 26/IX	23.0	57	753	,, ,,	9.0		
7	1935, 10/X	22.0	47	767	schönes Wetter	4.5	ca. 50	−3.8
8	,, , 12/X	24.0	54	764	,, ,,	3.5		
9	,, , 16/X	22.5	58	764	trübes Wetter	7.0		
10	,, , 21/X	22.0	47	768	sehr schönes W.	7.0		
11	1935, 30/X	21.0	48	763	schönes Wetter	5.0	ca. 50	−4.6
12	,, , 31/X	20.0	43	766	sehr schönes W.	6.0		
13	,, , 2/XI	19.0	52	769	,, ,, ,,	7.5		
14	1936, 29/I	7.0	63	761	trübes Wetter	6.0	ca. 50	−3.6
15	,, , 14/II	9.0	57	764	,, ,,	7.0		
16	,, , 17/II	9.0	65	762	,, ,,	7.0		
17	1936, 22/VI	30.0	64	759	trübes Wetter	3.5	125	−0.8
18	1936, 27/VI	28.0	58	762	trübes Wetter von Zeit zu Zeit kleiner Regenfall	5.0	130	−2.8
19	1936, 29/VI	28.0	76	ca. 760	trübes Wetter mit leichtem Regenfall	4.5	100	−1.8
20	1936, 2/VII	20.0	88	ca. 760	Regenwetter	5.0	135	−3.0
21	1936, 6/VII	20.0	87	760	Regenwetter	ca. 3.0	90	−4.4
22	1936, 8/VII	23.0	85	764	Regenwetter	ca. 3.0	80	−3.8
							Mittel	−3.7

Zwischen diesem Flaschensystem und der Wasserstrahlpumpe wurde immer eine mit konzentrierter Schwefelsäure beschickte grosse Waschflasche (S in den Abb. a und b) eingeschaltet, um die Rückdiffusion der Feuchtigkeit aus der Pumpe in die Flaschen zu verhindern. Beim Versuch Nr. 1 setzten wir in der Praxis jeder Reihe noch eine Flasche hinzu, so dass nun jede dieser drei Reihen aus drei Flaschen bestand. Da aber in diesen zugesetzten dritten Flaschen fast kein Wasser kondensiert gefunden wurde, haben wir sie in den späteren Versuchen Nr. 2 bis 13 fortgelassen. In den Versuchen Nr. 14 bis 16, wo die Strömungsgeschwindigkeit sehr klein war, konnten wir ohne Gefährdung des Resultates von der Anordnung mit zwei hintereinander verbundenen Flaschen absehen. Auf diese Weise gelang es uns, die atmosphärische Feuchtigkeit vollständig kondensiert im Flaschensystem anzusammeln. Aber da die Menge des kondensierten Feuchtigkeitswassers bei einem Versuch, der durchschnittlich einige Stunden dauerte (vgl. 7. Reihe der Tabelle) nur 10 bis 15 c.c. betrug, wurden einige Proben, die unter den fast gleichen Bedingungen gesammelt worden, vereinigt, das Gemenge gereinigt und zur Dichtemessung verwendet.

Bei den späteren Versuchen Nr. 17 bis 22 wurde dagegen bei jedem einzelnen Experiment eine zur Dichtemessung genügende Menge des Feuchtigkeitswassers gesammelt, indem wir doppelt so viele Kondensationsflaschen wie früher benutzten und die Strömungsgeschwindigkeit der Luft so gross wie möglich machten. Zwölf Flaschen wurden, wie Schema Abb. c zeigt, in sechs parallelen Reihen von je untereinander verbundenen Flaschen angeordnet und von aussen mit Eis gekühlt. Durch diese Flaschen wurde die ausserhalb des Zimmers durch ein kleines Flügelgebläse eingesaugte atmosphärische Luft geleitet. Die aus diesen Flaschen strömende Luft leiteten wir noch durch eine grosse 25 cm. hohe und 5 cm. weite Glasflasche (F in der Abb. c), die von aussen mit einem Kohlensäureschnee-Gemisch gekühlt wurde. Mittels dieser Anordnung gewannen wir bei mehrstündiger Durchströmung der Luft durchschnittlich 100 g. Feuchtigkeitswasser (vgl. 7. und 8. Reihe der Tabelle). Von dieser Wassermenge wurden 60 bis 70% in der vorderen Abteilung 20 bis 30% in der hinteren des mit Eis gekühlten Flaschensystems und der Rest von 10% in der letzten mit Kohlensäure gekühlten Flasche F gefunden. Eventuell schalteten wir zu allerletzt noch eine mit Kohlensäure gekühlte Flasche ein. Doch fanden wir in dieser Flasche selbst nach halbstündiger Durchleitung von Luft kein Kondensat. Dies überzeugte uns, dass die atmosphärische Feuchtigkeit durch unsere Anordnung fast vollständig kondensiert wurde. Eine minimale Fraktionierung des Feuchtigkeitswassers, zu der es eventuell durch unvollständige Kondensation kommen kann, übt

wegen des kleinen Dichteunterschiedes zwischen Feuchtigkeits- und gewöhnlichem Wasser keinen merklichen Einfluss auf das Endresultat aus.

Reinigung und Dichtemessung des Feuchtigkeitswassers. Das auf die obenangegebene Weise gesammelte Feuchtigkeitswasser wurde zunächst entweder durch Destillation (bei Nr. 1 bis 16) oder durch Filtration (bei Nr. 17 bis 22) von beigemengten Stäubchen befreit und dann unter Zusatz von Kaliumpermanganat und Ätzkali drei bis fünf Stunden lang sieden lassen. Dann wurde das Wasser aus dieser Lösung vollständig abdestilliert. Das abdestillierte Wasser wurde durch weitere dreimalige Destillation völlig gereinigt, und zwar wurde die erste Destillation unter Zusatz einer geringen Menge Phosphorpentoxyd, die zweite unter Zusatz von Bariumhydroxyd in kohlensäurefreiem Luftstrom und die letzte ebenfalls in kohlensäurefreier Luft ohne jeden Zusatz aber unter Verwendung eines Quarzkühlers durchgeführt. Das spezifische Gewicht des so gereinigten Feuchtigkeitswassers wurde nach der Schwebemethode mittels eines Quarzschwimmers mit dem des Osaka-Leitungswassers bei 9.5°C. verglichen. Die Messgenauigkeit dürfte $\pm 0.5\,\gamma$ betragen. Den dabei gefundenen Dichteunterschied ΔS zwischen dem Feuchtigkeitswasser und dem Osaka-Leitungswasser haben wir in der 9. Vertikalreihe der Tabelle wiedergegeben. Danach ist das Feuchtigkeitswasser um 1 bis 7 γ, durchschnittlich um $4\,\gamma$ leichter als gewöhnliches Wasser.

Diskussion. Nimmt man an, dass die atmosphärische Feuchtigkeit durch die Verdampfung des Wassers auf der Erdoberfläche entsteht, so ist ohne weiteres zu erwarten, dass das Feuchtigkeitswasser spezifisch leichter als gewöhnliches Wasser sein muss. Was aber den quantitativen Dichteunterschied zwischen beiden anbetrifft, so ist die Sache insofern kompliziert, als die Dichte des Feuchtigkeitswassers bzw. dessen Gehalt an schwerem Wasser von vielen Faktoren abhängt. Dabei kommen zunächst die Bedingungen bei der Entstehung der Feuchtigkeit in Frage. Wenn z.B. gewöhnliches Süsswasser bei gewöhnlichen Temperaturen (5–35°C.) verdampft, muss die Dichte der ersten Fraktion um 3 bis $4\,\gamma$ kleiner als gewöhnliches Wasser sein, das entsprechende Destillat aus Meerwasser dagegen um 2 bis $3\,\gamma$, weil bekanntlich Meerwasser durchschnittlich um $1.5\,\gamma$ schwerer als Süsswasser ist.[1] Es handelt sich dabei aber um einen idealen Fall, wo die Verdampfung genügend langsam isothermisch verläuft. Nimmt die Verdampfungsgeschwindigkeit zu, so muss sich die resultierende Dichteabnahme des Destillats dementsprechend verändern.[2] Mit der Erhöhung der Temperatur bei der Ver-

(1) H. E. Wirth, T. G. Thompson und C. L. Utterback, *J. Am. Chem. Soc.*, **57** (1935), 400; *Nature*, **135** (1935), 662.

(2) Darüber, ob es sich dabei um die Vergrösserung oder Verminderung der Grösse der Dichteabnahme des Destillats handelt, kann man a priori nichts Bestimmtes sagen.

dampfung verringert sich offenbar die Dichteabnahme des Destillats und vice versa. Ausser den ebengeschilderten bei der Entstehung des Wassers in Frage kommenden Bedingungen kann auch folgender Umstand, auf den schon Eucken und Schäfer[3] hingewiesen haben, den Gehalt des Feuchtigkeitswassers an schwerem Wasser beeinflussen. Wenn z.B. ein Teil der Feuchtigkeit durch Regenfall abscheidet, muss der zurückbleibende Teil infolge fraktionierter Kondensation ärmer an schwerem Wasser, d.h. leichter werden. Durch das Zusammenwirken aller der ebenangegebenen Faktoren wird die Dichte des Feuchtigkeitswassers bestimmt. Die bei unseren Versuchen gefundene Grösse und Variation der Dichteabnahme des Feuchtigkeitswassers dem gewöhnlichen Wasser gegenüber lässt sich mit Hilfe der obenangeführten Faktoren genügend erklären.

Einige Autoren fanden bei ihren Versuchen[4] das *frisch* gefallene Schneewasser durchschnittlich um 2 bis 3 γ leichter als gewöhnliches Wasser, und es liegen für diese Erscheinung bereits einige Erklärungsversuche vor.[5] Aber bei unseren Versuchen ist ohne weiteres zu erwarten, dass das Schneewasser eine um einige γ kleinere Dichte als gewöhnliches Wasser besitzen muss, falls man annimmt, dass Schnee dadurch entsteht, dass atmosphärische Luft aus irgendeiner Ursache plötzlich abgekühlt und infolgedessen das Feuchtigkeitswasser, das sie enthält, fast restlos abgeschieden wird.

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(3) A. Eucken und K. Schäfer, *Göttinger Nachrichten, neue Folge*, **1935**, 137.

(4) E. Baroni und A. Fink, *Monatsh.*, **65** (1935), 386; *ibid.*, **67** (1936), 131, 193; A. Eucken und K. Schäfer, *Göttinger Nachrichten, neue Folge*, **1935**, 109, 137; W. A Alexander und L. A. Munro, *Can. J. Research*, B, **14** (1936), 47; M. Harada und T. Titani, dieses Bulletin, **10** (1935), 206, 263.

(5) Vgl. die Mitteilungen von A. Eucken und K. Schäfer in Fussnote (3) sowie die von M. Harada und T. Titani in Fussnote (4).

The Viscosity of Mixed Salt Solutions.

By Tetsuya ISHIKAWA.

(Received November 25th, 1936.)

From the extensive work on the viscosity of binary liquid mixtures and of solutions of solids in liquids for these ten years[1], the author has come to the conclusion that his fundamental formula defines an ideal mixture law or a physical mixture law. The formula runs:

$$\eta = \frac{\eta_1}{1+K\frac{z_m}{1-z_m}} + \frac{\eta_2}{1+\frac{1}{K}\frac{1-z_m}{z_m}},$$

where η_1, η_2, and η are the viscosities of component 1, 2, and the mixture; z_m a formal molar fraction of component 2 in the mixture; and K the characteristic constant for the mixture or, precisely saying, the ratio of the characteristic constant of component 2 to that of component 1.

Since this formula represents the true viscosity on mixing two chemically indifferent liquids for the whole range of concentration, and that on dissolving a non-reactive solid in a liquid up to its saturation, one may easily arrive at the precognition that the same law will hold for the viscosity of mixed salt solutions, provided that the component solutions which do not react have a common solvent and the composition of the mixture has a constant total concentration throughout the admixture. If we take c_1 and c_2 the concentrations of two solutions in the mixture, e.g. in gram-mole per 1000 g. of solvent respectively in order to make this sum c, total concentration, to keep a constant by mixing appropriate weights of primary solutions of concentration c, $(1-z_m)$ and z_m in the above formula may be replaced by c_1/c and c_2/c respectively, since the quantity of solvent is unchanged before and after mixing. Naturally, K which means here the ratio of the characteristic constants of two solutions of a common solvent may take a value not so much differing from unity especially for dilute salt solutions.

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(1) This Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155; **10** (1935), 153, 248; **11** (1936), 8, 64.

There have been a few measurements on the viscosity on mixing salt solutions under the above precaution. Stearn[2] first measured the relative viscosities of the aqueous solution pairs of NaCl—KCl and NaI—KI; Ruby and Kawai[3] made careful measurements, their precision being not less than one part in two thousand, on the relative viscosities of binary and ternary mixtures of HCl, KCl, and NaCl at the concentrations of 0.5, 1.0, 2.0, and 4.0 gram-mole per 1000 g. of water, and pointed out that the viscosities of binary mixtures of these electrolytes are consistently less than values computed by the rule of mixtures (additivity with respect to molar concentration), save in the cases of the most dilute mixtures; Tollert[4] measured the viscosities of similar pairs of electrolyte solutions at only one composition and tested with fair success his own formula, $\eta = \sqrt{\eta_1\eta_2}(1+A'\sqrt{\gamma_1\gamma_2})$, in which γ_1 and γ_2 denote the concentrations of components in val/litre, and A' a specific constant of the mixture depending on temperature alone; and recently Banchetti[5] examined, with the data of his own for the solution pairs of $K_2SO_4-ZnSO_4$ and urethane—urea and of those of others cited above, the formulas of Kendall, Bingham, and Tollert, and found that they all failed to represent the actual viscosities of mixtures at concentrated salt solutions. He referred the present author's paper on the viscosity of aqueous solutions of electrolytes[6], but unfortunately he did not attempt to test the latter's fundamental formula given above. The present paper is, therefore, contributed to the study in this line as an appendix to the author's foregoing papers on the viscosity of binary mixtures.

The data employed in the following verification of the author's formula are adopted from the values observed by Banchetti and by Ruby and Kawai.

As seen from Tables 1, 2, 3, 4, and 5, in which z_m denotes a fractional concentration of the second salt solution in each pair of total concentration c in gram-mole per 1000 g. of water, the divergences of the calculated values from the observed values are all less than 2×10^{-3} and lie within the experimental error limit, so that the coincidence is said to be extremely satisfactory. For closer investigation of K in these pairs, however, we must have more accurate measurements.

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(2) A. E. Stearn, *J. Am. Chem. Soc.*, **44** (1922), 670.
(3) C. E. Ruby and J. Kawai, *J. Am. Chem. Soc.*, **48** (1926), 1120.
(4) H. Tollert, *Z. physik. Chem.*, A, **172** (1935), 129.
(5) A. Banchetti, *Gazz. chim. ital.*, **64** (1934), 229; **65** (1935), 159; **66** (1936), 446.
(6) This Bulletin, **10** (1935), 153.

Table 1. Urethane aq. (1)—Urea aq. (2), 25°C. (Banchetti).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0890	—		1.1755	—	
0.25	1.0713	1.0712	1	1.1416	1.1412	4
0.50	1.0536	1.0537	−1	1.1071	1.1071	0
0.75	1.0363	1.0363	0	1.0731	1.0731	0
1.00	1.0191	—		1.0393	—	
	$K = 1.021$			$K = 1.009$		

Table 2. $ZnSO_4$ aq. (1)—K_2SO_4 aq. (2), 25°C. (Banchetti).

z_m	$c = 0.1$			$c = 0.5$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.00	1.0662	—		1.3656	—	
0.25	1.0548	1.0550	−2	1.2932	1.2930	2
0.50	1.0442	1.0441	1	1.2267	1.2269	−2
0.75	1.0337	1.0336	1	1.1662	1.1668	−6
1.00	1.0234	—		1.1115	—	
	$K = 1.067$			$K = 1.201$		

Table 3. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0317	—		1.0617	—	
0.2	1.0250	1.0248	2	1.0483	1.0481	2
0.4	1.0182	1.0180	2	1.0351	1.0350	1
0.6	1.0112	1.0114	−2	1.0221	1.0224	−3
0.8	1.0048	1.0048	0	1.0102	1.0102	0
1.0	0.9983	—		0.9985	—	
	$K = 1.037$			$K = 1.096$		

Table 3_2. HCl aq. (1)—KCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.1210	—		1.2378	—	
0.2	1.0972	1.0968	4	1.2068	1.2052	16
0.4	1.0735	1.0734	1	1.1713	1.1709	4
0.6	1.0506	1.0508	−2	1.1341	1.1349	− 8
0.8	1.0285	1.0288	−3	1.0954	1.0970	−16
1.0	1.0076	—		1.0570	—	
	$K = 1.085$			$K = 0.881$		

Table 4_1. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	0.9983	—		0.9985	—	
0.2	—			1.0166	1.0166	0
0.4	1.0169	1.0169	0	1.0352	1.0351	1
0.6	1.0264	1.0264	0	1.0537	1.0541	−4
0.8	—			1.0736	1.0736	0
1.0	1.0456	—		1.0936	—	
	$K = 0.974$			$K = 0.940$		

Table 4_2. KCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0076	—		1.0570	—	
0.2	1.0431	1.0435	−4	1.1309	1.1308	1
0.4	1.0811	1.0812	−1	1.2118	1.2121	−3
0.6	1.1209	1.1209	0	1.3022	1.3019	3
0.8	1.1632	1.1626	6	1.4030	1.4019	11
1.0	1.2065	—		1.5136	—	
	$K = 0.882$			$K = 0.771$		

Table 5_1. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 0.5$			$c = 1.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.0317	—		1.0936	—	
0.2	—			1.0862	1.0866	−4
0.4	1.0369	1.0370	−1	1.0797	1.0799	−2
0.6	1.0398	1.0397	1	1.0736	1.0736	0
0.8	—			1.0676	1.0675	1
1.0	1.0456	—		1.0617	—	
	$K = 0.914$			$K = 0.888$		

Table 5_2. HCl aq. (1)—NaCl aq. (2), 25°C. (Ruby and Kawai).

z_m	$c = 2.0$			$c = 4.0$		
	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$	$\eta_{obs.}$	$\eta_{calc.}$	Difference $\times 10^4$
0.0	1.2065	—		1.5136	—	
0.2	1.1870	1.1865	5	1.4484	1.4474	10
0.4	1.1684	1.1681	3	1.3877	1.3875	2
0.6	1.1509	1.1512	−3	1.3329	1.3331	−2
0.8	1.1350	1.1355	−5	1.2834	1.2834	0
1.0	1.1210	—		1.2378	—	
	$K = 0.818$			$K = 0.792$		

The comparison among the results with other formulas which were given by Banchetti is reproduced here. In Tables 6 signify Δ_M, Δ_K, Δ_B, Δ_L, Δ_S, and Δ_I the average divergences of the observed and calculated viscosities by use of the formulas of viscosity linearity, Kendall's cube-root, Bingham, and Kendall's logarithmic, Banchetti, and Ishikawa.

Besides the formulas quoted above there have been proposed more than ten formulas. For the aid of further comparison, therefore, I will give severe tests for the validity of the hitherto existing formulas with two typical ideal mixtures in the classical meaning (mixtures in which there occurs no volume change on mixing), C_2H_5OH—i-C_3H_7OH[7] and $C_2H_4Br_2$—$C_2H_4Cl_2$[8].

(7) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **29** (1925), 727.
(8) W. MacFarlane and R. Wright, *J. Chem. Soc.*, (**1933**), 114.

Table 6. The Validity of Various Formulas for Solution Pairs.

Pair	Deviations × 10^3					
	Δ_M	Δ_K	Δ_B	Δ_L	Δ_S	Δ_I
$c = 0.5$						
HCl – KCl	−0.5	−0.4	−0.2	−0.3	−1.6	0.1
KCl – NaCl	−0.3	−0.1	0.2	−0.1	0.6	0.0
HCl – NaCl	−0.3	−0.3	−0.3	−0.3	−1.2	0.0
$c = 1.0$						
HCl – KCl	−1.7	−1.4	−0.8	−1.2	−1.7	0.0
KCl – NaCl	−1.3	−0.6	0.7	−0.3	0.7	−0.1
HCl – NaCl	−0.7	−0.7	−0.6	−0.7	−0.5	−0.1
$c = 2.$						
HCl – KCl	−2.3	−1.3	0.5	−0.4	1.3	0.0
KCl – NaCl	−5.6	−3.0	2.2	−1.7	7.0	0.0
HCl – NaCl	−3.7	−3.3	−2.4	−3.0	2.9	0.0
$c = 4.0$						
HCl – KCl	4.0	6.3	10.0	7.2	19.7	−0.1
KCl – NaCl	−23.0	−12.2	8.0	−7.7	33.5	0.3
HCl – NaCl	−11.4	−8.2	−1.6	−6.5	22.6	0.2

(1) Bingham[9] (1906): $\varphi = \varphi_1(1-z_v)+\varphi_2 z_v$.

(2) Drucker and Kassel[10] (1911): $\varphi = \varphi_1(1-z)+\varphi_2 z$.

(3) Dolezalek[11] (1913): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_v)+\eta_2^{\frac{1}{2}} z_v$.

(4) Kendall[12] (1913): $\log \eta = (1-z_m)\log \eta_1 + z_m \log \eta_2$.

(5) Ssachanov and Rjachowski[13] (1914):

$$\eta = \eta_1(1-z_m)^2+\eta_2 z_m^2+n\sqrt{\eta_1\eta_2}(1-z_m)z_m .$$

(6) Ssachanov and Rjachowski[14] (1915):

$$\eta = \eta_1(1-z_m)+\eta_2 z_m - k(1-z_m)z_m , \quad k = \eta_1+\eta_2-n\sqrt{\eta_1\eta_2} .$$

(9) E. C. Bingham, *Am. Chem. J.*, **35** (1906), 195.
(10) K. Drucker and R. Kassel, *Z. physik. Chem.*, **76** (1911), 367.
(11) F. Dolezalek and A. Schulze, *Z. physik. Chem.*, **83** (1913), 45.
(12) J. Kendall, *Medd. Vetenskapzakad. Nobelinst.*, **2** (1913), No. 25, 1.
(13) A. Ssachanov and N. Rjachowski, *Z. physik. Chem.*, **86** (1914), 529.
(14) A. Ssachanov and N. Rjachowski, *J. Russ. Phys.-Chem. Soc.*, **47** (1915), 113.

(7) Kendall[15] (1917): $\eta^{\frac{1}{3}} = \eta_1^{\frac{1}{3}}(1-z_m)+\eta_2^{\frac{1}{3}}z_m$.

(8) Drucker[16] (1918): $\varphi d = \varphi_1 d_1(1-z_m)+\varphi_2 d_2 z_m$.

(9) Meyer and Mylius[17] (1920): $\varphi = \varphi_1\frac{b_1}{b}(1-z)+\varphi_2\frac{b_2}{b}z$.

(10) Macleod[18] (1924):

$$\eta = \eta_1\frac{x_1}{x}(1-z_m)+\eta_2\frac{x_2}{x}z_m,\quad x = x_1(1-z_v)+x_2 z_v.$$

(11) Bateman and Baechler[19] (1926): $\eta^{(1-z_v)+kz_v} = \eta_1^{(1-z_v)}+\eta_2^{kz_v}$.

(12) Ishikawa[20] (1929): $\eta = \dfrac{\eta_1}{1+K\dfrac{z_m}{1-z_m}}+\dfrac{\eta_2}{1+\dfrac{1}{K}\dfrac{1-z_m}{z_m}}$.

(13) Bingham and Brown[21] (1932):

$$\varphi = \varphi_1(1-z_v)+\varphi_2 z_v - K(z-z_v)(v_1-v_2).$$

(14) Cragoe[22] (1933): $\eta v = Ae^{\frac{B}{L'}}$, $L' = L_1'(1-z)+L_2'z$.

(15) Lautié[23] (1935): $\eta^{\frac{1}{2}} = \eta_1^{\frac{1}{2}}(1-z_m)+\eta_2^{\frac{1}{2}}z_m$.

In these formulas, η and φ and those with suffixes 1 and 2 are the viscosities and fluidities of the mixture and components 1 and 2 respectively; v and d and those with suffixes the specific volumes and densities of the mixture and the components respectively; and z, z_v, and z_m a weight, volume, and molar fraction of component 2 respectively. For an explanation of the other symbols used the reader is referred to the original papers.

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(15) J. Kendall and K.P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.
(16) C. Drucker, *Z. physik. Chem.*, **92** (1918), 287.
(17) J. Meyer and B. Mylius, *Z. physik. Chem.*, **95** (1920), 349.
(18) D. B. Macleod, *Trans. Faraday Soc.*, **20** (1924), 348.
(19) E. Bateman and R. Baechler, *Proc. Am. Wood-Preserver's Assoc.*, (**1926**), 89.
(20) T. Ishikawa, this Bulletin, **4**, (1929), 5.
(21) E. C. Bingham and D. F. Brown, *J. Rheol.* **3** (1932), 95.
(22) C. S. Cragoe, *Proc. World Petroleum Congr., London F*, (**1933**), 529.
(23) R. Lautié, *Bull. soc. chim.*, [5], **2** (1935), 2187.

Table 7. The Validity of Various Formulas for the Pair of C_2H_5OH (1)—i-C_3H_7OH (2), 25°C. (Parks and Kelley).

Formula	$\begin{cases} z = 0.1639 \\ z_v = 0.1646 \\ z_m = 0.131 \end{cases}$	$\begin{cases} z = 0.3311 \\ z_v = 0.3321 \\ z_m = 0.275 \end{cases}$	$\begin{cases} z = 0.5013 \\ z_v = 0.5025 \\ z_m = 0.435 \end{cases}$	$\begin{cases} z = 0.6640 \\ z_v = 0.6649 \\ z_m = 0.607 \end{cases}$	$\begin{cases} z = 0.8277 \\ z_v = 0.8285 \\ z_m = 0.786 \end{cases}$	Constants used
	Deviations × 10^5 (with respect to η)					
(1)	11	18	29	32	21	
(2)	11	19	29	33	22	
(3)	−37	−68	−83	−80	−62	
(4)	8	11	19	19	10	
(5)	2	1	3	−3	−4	$n = 1.942$
(6)	2	1	3	−3	−4	$k = 0.00241$
(7)	−2	−7	−5	−7	−10	
(8)	30	58	87	94	79	
(9)	−4	0	4	0	−23	$\begin{cases} b_1/b = 0.989 \\ b_2/b = 0.970 \end{cases}$
(10)	—	—	—	—	—	
(11)	3	2	5	5	−1	$k = 0.807$
(12)	0	−1	3	−1	−1	$K = 0.777$
(13)	2	−2	−1	−1	−5	
(14)	−5	1	4	7	−6	$K = 1.65 \times 10^5$
(15)	−8	−16	−19	−24	−18	

see errata V. 17, P. 952

Table 8. The Validity of Various formulas for the Pair of $C_2H_4Br_2$ (1)—$C_2H_4Cl_2$ (2), 25°C. (MacFarlane and Wright).

Formula	$z=0.1005$, $z_v=0.1636$, $z_m=0.1750$	$z=0.2404$, $z_v=0.3686$, $z_m=0.3875$	$z=0.3510$, $z_v=0.4860$, $z_m=0.5059$	$z=0.4997$, $z_v=0.6365$, $z_m=0.6550$	$z=0.6504$, $z_v=0.7659$, $z_m=0.7791$	$z=0.7492$, $z_v=0.8396$, $z_m=0.8501$	Constants used
	Deviations $\times 10^5$ (with respect to η_i)						
(1)	47	57	53	43	29	12	
(2)	−37	−66	−57	−47	−36	−32	
(3)	−36	−46	−53	−42	−31	−30	
(4)	1	−1	−1	3	1	−6	
(5)	−4	−6	0	5	4	−3	$n=1.867$
(6)	−4	−6	0	5	4	−3	$k=0.00299$
(7)	−15	−26	−25	−19	−13	−17	
(8)	−32	−54	−52	−45	−33	−32	
(9)	58	2	0	−3	0	−4	$b_1/b=1.08$, $b_2/b=1.02$
(10)	−1	−6	−7	−3	−3	−6	$x_1=0.0628$, $x_2=0.0911$
(11)	0	−2	−1	2	2	−6	$k=1.08$
(12)	2	−2	−1	1	−1	−7	$K=1.43$
(13)	−51	−86	−83	−70	−48	−46	
(14)	7	−1	2	1	−1	−10	$K=92.7$
(15)	−24	−39	−39	−29	−21	−22	

see errata V. 13, 253

The superiority of the Ishikawa formula above the rest is readily accepted from the strict coincidences equably obtained in these examples as shown in Tables 6, 7, and 8.

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On the End-Point Voltage of the Lead-Acid Storage Cell.

By Kyôji KINOSHITA.

(Received November 27th, 1936.)

The terminal voltage of a lead-acid storage cell falls, gradually, in the course of discharge and finally the discharge must be terminated at the proper value of the voltage, which is called the end-point voltage of the cell. Abolition of the end-point voltage is said to result in the formation of crystalline lead sulphate in the active material of the plates, and reduces the capacity and life of the electrodes.

Vinal[1], Lyndon[2], and Nakamura[3] studied the relations between the end-point voltage and the discharge hour rate of the cell. The following experiments have been undertaken on this subject.

Table 1.

t_0-t (min.)	e (volt)	C (%)
$t_0 = 275$	2.038	100
274	1.960	99.6
273	1.962	99.3
272	1.966	98.8
269	1.968	97.8
264	1.968	96.1
259	1.968	94.2
254	1.970	92.4
249	1.966	90.6
234	1.962	85.2
219	1.960	79.6
199	1.958	72.4
179	1.948	65.2
149	1.940	54.2
119	1.928	43.3
89	1.920	32.2
59	1.900	21.4
29	1.866	10.6
14	1.838	5.1
9	1.816	3.3
4	1.770	1.5
3	1.756	1.1
2	1.722	0.7
1	1.642	0.4
0	1.480	

Experimental. The cells under examination were connected in series and several cycles of charge and discharge were made by the constant currents of 1.5 amp., 2.0 amp., 2.5 amp., and 3.0 amp. The end-point voltage was taken at about 1.3 volts, while that specified by the maker of the cells was 1.8 volts. As such discharge will cause the formation of crystalline lead sulphate in the active material, the cell was charged as soon as possible after the discharge had been terminated.

One example of change of the terminal voltage with time is tabulated in Table 1. In this table t_0 denotes the total time of discharge and t the time at which the terminal voltage is e. The values of C is defined as follow:

$$C = \frac{t_0-t}{t_0} \times 100 .$$

(1) Vinal, "Storage batteries," (1924), 177.
(2) Lyndon, "Storage battery engineering," (1911), 91.
(3) Nakamura, *Bull. Dept. Railways, Govt. Japan*, **18** (1930), 1-26.

The values of t_0-t in the table will be proportional to the remaining capacity of the cell provided the discharge is undertaken at a constant current. Consequently, the value of C indicates the percentage ratio of the remaining capacity to the total capacity of the cell.

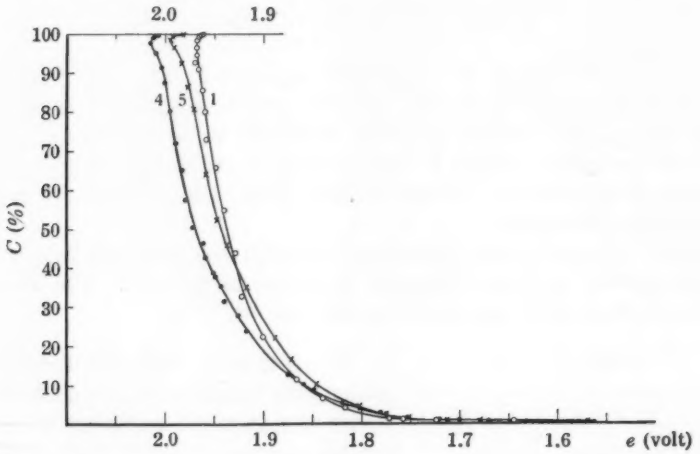

Fig. 1.

The relation between C and e on the three different types of the cells are represented in Fig. 1. As seen from Fig. 1, the terminal voltage of the cell No. 4 is higher than the others in the early stage of the discharge but it falls rather quickly. The terminal voltage of the cell No. 1 is lower at first but it falls slowly and finally takes the highest value among the three, when C falls to about 10. The cell No. 5 shows an intermediate value until C falls to about 40, and becomes the lowest when it falls under 40.

The discharge capacities of these three cells are shown in Table 2.

Table 2. (2.0 amp. discharge)

Cell No.	Discharge hours	Discharge capacity
1	4 h. 36 m.	9.2 a.h.
4	6 41	13.4
5	4 18	8.6

From the above results we see that the terminal voltage e of the cell having the larger capacity is not always higher than that of the cell having the smaller capacity, the value of C being the same. It may be an interesting fact that the C-e curve shows some characteristic nature of the cell.

The C-e curves obtained by different discharge currents on the cells of

the same type are shown in Fig. 2. The curves correspond to the discharge current of 1.5 and 3 amp. As is seen from this figure the terminal voltage is higher in the case of a weaker discharge current than the case of stronger

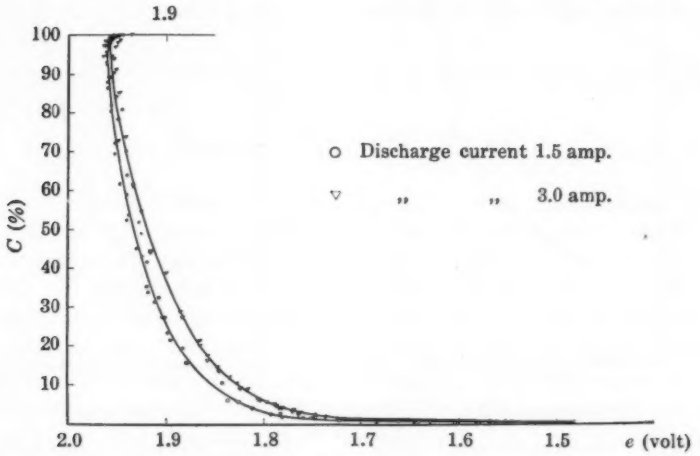

Fig. 2.

discharge current provided the value of C is the same. Consequently, if there be a definite value of C at which the formation of the crystalline lead sulphate occurs, the end-point voltage in the case of a smaller discharge current must be taken higher than in the case of a larger discharge current.

Now the values of $\log C$ and $\log e$ are delineated in Fig. 3, Fig. 4, Fig. 5, and Fig. 6. These figures correspond to the data obtained by the discharge currents of 1.5, 2.0, 2.5, and 3.0 amperes, respectively.

As seen from these figures the relation between $\log C$ and $\log e$ is almost linear in the upper part of the figures, while the curves are concave to the C axis at the lower part. We see, moreover, that the linear part becomes the more predominate in the case of the higher discharge current. The linear part of the curves may be represented by the following formula:

$$\log C = m \log e + \log k \qquad (1),$$

where m and k are the constants. This equation can be transformed into the following forms:

$$C = k\, e^m \quad (2) \qquad \text{or} \qquad e = K\, C^n \quad (3), \quad \text{where } n = 1/m.$$

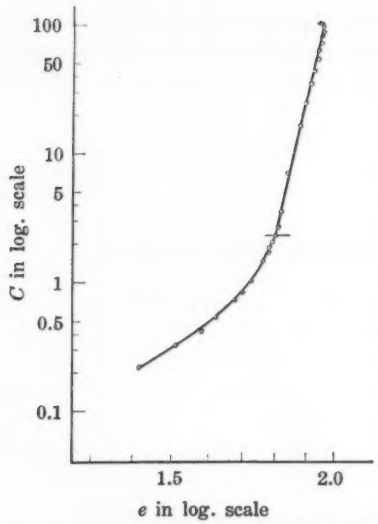

Fig. 3. Discharge current 1.5 amp.

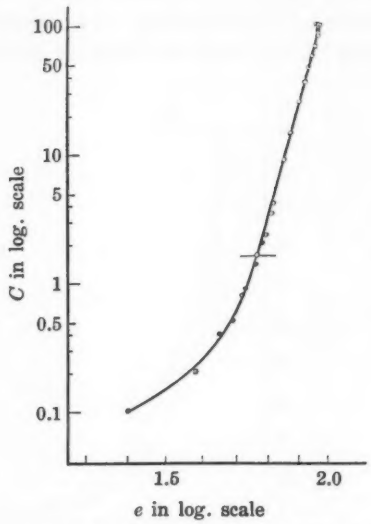

Fig. 4. Discharge current 2.0 amp.

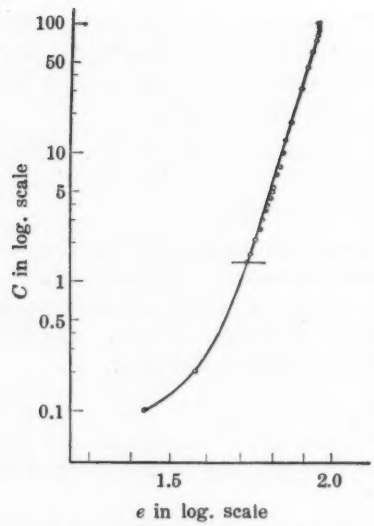

Fig. 5. Discharge current 2.5 amp.

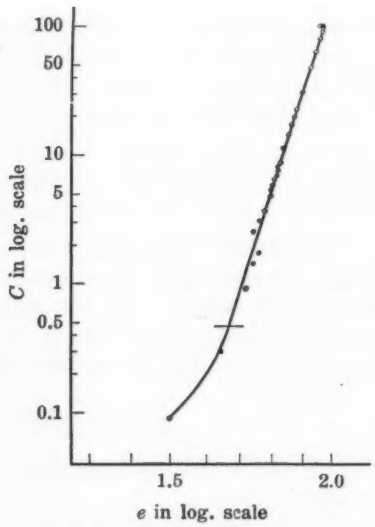

Fig. 6. Discharge current 3.0 amp.

From equation (3) it follows that the terminal voltage e of the cell is proportional to the n-th power of the percentage of the remaining active material out of the total active material, which should be consumed at the end of the discharge. Namely, the terminal voltage of the cell may be said to be proportional to the n-th power of the concentration of remaining active material in the plate.

It was known that the terminal voltage of the cell can be represented by the following equations:

$$e = E+IW \quad \text{in charge}; \quad \text{and} \quad e = E-IW \quad \text{in discharge},$$

where E is the electromotive force of the cell in volts, I the charge and discharge current in amperes, and W the internal resistance in ohms. The internal resistance of the cell is said to be very small except at the end of the discharge. It follows that the variation of the terminal voltage of the cell in the discharging state is mainly due to the variation of E by polarization. The polarization caused by the variation of the concentration of sulphuric acid at the electrode will be the most important factor. But the existence of the relation (3) shows that the variation of the value of C has some relation to the variation of e. The examination of the nature of the cell in the course of discharge may be made from this point of view.

As soon as the discharge is begun, the consumption of sulphuric acid at the electrodes is expected, and there occurs the reduction of the concentration of acid in the pores of the electrodes. The change of concentration of the acid will bring about the fall of terminal voltage by polarization. After a while sulphuric acid will diffuse into the pores from outside the electrodes, until finally the supply and the consumption of the acid become stationary. At this stage the chief cause which effects the fall of terminal voltage may be considered to be the variation of C within the active material of the plates. At the end of the discharge the pores of the plates are clogged by the lead sulphate which has formed during the course of discharge. Consequently, the supply of the acid into the pores may be interrupted and there occurs a sudden fall of the terminal voltage. The linear relation between $\log C$ and $\log e$ can no more be seen in this stage of the discharge. The fact that the curvature of the lower part of the $\log C$-$\log e$ curve becomes more gradual as the discharge current becomes large is the result of the gradual fall of the terminal voltage due to the steep concentration gradient between the electrolytes in and out of the pores produced by the superficial functioning of the plate.

From the above considerations, the ranges where the relation (3) holds between C and e may be the most favourable condition of the plates, for the

value of e varies according to the polarization due to the variation of the strength of acid and that of the value of C, these two being in equilibrium.

It follows that the value of e, where the relation (1) does no more hold between C and e may be the most reasonable end-point voltage of the cell.

Table 3.

No. of the cell	Discharge current 1.5 amp.		Discharge current 2.0 amp.		Discharge current 2.5 amp.		Discharge current 3.0 amp.	
	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)	C (%)	e (volt.)
No. 1	1.55	1.785	1.30	1.752	1.00	1.720	1.03	1.708
No. 2	1.91	1.784	1.47	1.757	1.50	1.745	1.20	1.715
No. 3	1.46	1.758	1.45	1.753	1.25	1.734	0.77	1.689
Mean	1.64	1.776	1.41	1.754	1.25	1.733	1.00	1.704

The values of C and e thus obtained by the diagrams, Fig. 3—Fig. 6 as examples, are tabulated in Table 3. The values of C and e tabulatad here are the mean values of nine discharges for one value of discharge current. In Fig. 7 these values of e are plotted against the discharge hour rate of the cell. The reasonable end-point voltage of the cell at 6-hour rate of discharge may be considered to be 1.784 volts.

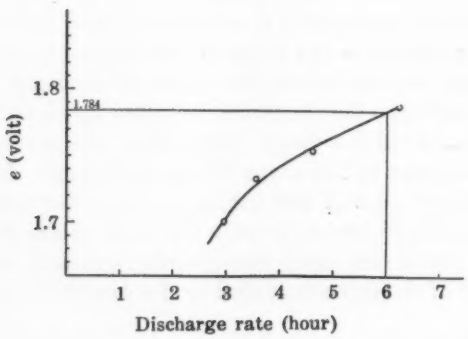

Fig. 7.

The equation (3) is analogous in form to Freundlich's formula for adsorption: $x = \alpha D^{\frac{1}{a}}$, where x denotes the amount of the solute adsorbed by 1 gram of the adsorbent, D the concentration of the solution in equilibrium with the adsorbent, and α and a are constants. If it be an ideal solution this formula coincides with Henry's partition law, and the value a becomes unity. By analogy the value of n in equation (3) may be considered to indicate the state of dispersion of the active material in the plate. If the active material of the plate forms a homogeneous solid solution with $PbSO_4$ the value of n in the equation (3) may become unity. In this case (3) will be transformed into the following form: $e = KC$. Namely, the terminal voltage of the cell is directly proportional to the concentration of the remaining active material in the plate. If the active material of the plate be colloidally dispersed into $PbSO_4$, e will be proportional to the n-th power of C. And if the active material of the plate behaves as a mere mass of PbO_2 or Pb, the value of n in the equation (3) will become naught, and the equation will takes the form: $e = \text{const.}$ In this case the terminal voltage of the cell only depends upon the active material used in the plate and will become quite independent of the concentration of the remaining active material.

As the results of above-mentioned analogy between the equation (3) and Freundlich's formula, the value of n in the equation (3) may be considered to represent the structural features of the plate.

In conclusion the author wishes to express his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advice throughout this experiments.

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A Theory of Surface Tension of Debye-Hückel Electrolyte.

By Kyozo ARIYAMA.

(Received June 1st, 1936.)

The present writer has recently proposed a comprehensible theory of adsorption of Debye-Hückel electrolyte.[1] It was found that a similar theory could be advanced to calculate the surface tension of Debye-Hückel electrolyte. Wagner's very elaborate mathematical theory of surface tension[2] which was later simplified by Onsager and Samaras[3] uses the theory of images near the boundary between water and air. Aside from a great mathematical difficulty, the use of theory of images in the atomic realm without justification is rather objectionable. Oka[4] recently formulated a very reasonable theory of surface tension of dilute solution of strong electrolyte and obtained an explicit expression for the change of surface tension with concentration of the solution in the liquid. The present paper[5] gives a very simple yet a quite reasonable methed of calculating the surface tension. The explicit formula is derived and compared with experiment quite satisfactory. The difference between Oka's value and the value that is given here is that Oka's value is exactly twice as large as that of the present author.

Consider a liquid which is in thermodynamic equilibrium with a vapor. We shall apply the thermographic principle to this system, then we obtain

$$dU = Td\eta + \sigma ds - pdV, \tag{1}$$

where U is the internal energy, η the entropy of the total system, σ the surface tension, and T, S, V and p stand for the usual meanings. Since U, the internal energy, is a function of T the temperature, V the volume, and S the surface of the liquid, we obtain

$$Td\eta = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial S} - \sigma\right)dS + \left(\frac{\partial U}{\partial V} + p\right)dV.$$

(1) This Bulletin, **11** (1936), 687.
(2) *Phys. Z.*, **25** (1924), 474.
(3) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.
(4) S. Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(5) The author was unaware of the Oka's paper at the time when he proposed a theory of adsorption of Debye-Hückel electrolyte. Oka's theory contains an integral which seems only approximately estimated, so it may change the result by a factor 2 or 3 if rigorously calculated.

The condition that $d\eta$ is an exact differential gives

$$\frac{\partial}{\partial S}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right)=\frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial S}-\sigma\right)\right]$$

or
$$U_s=\sigma-T\frac{d\sigma}{dT}, \tag{2}$$

where
$$U_s=\frac{\partial U}{\partial S},$$

If we consider a solution of strong electrolyte, we obtain for small change in the surface energy U_s the following equation

$$\Delta U_s=\Delta\sigma-T\frac{d}{dT}\Delta\sigma, \tag{3}$$

where $\Delta\sigma$ is corresponding small change in the surface tension. Solving equation (3) for $\Delta\sigma$, we get

$$\Delta\sigma=-T\int_{\infty}^{T}\frac{\Delta U_s}{T^2}dT. \tag{4}$$

Here the intergration constant is determined so as to make $\Delta\sigma/T$ vanish at $T=\infty$.

We shall now apply the kinetic theory for the calculation of ΔU_s. If we consider a special case, that is, a dilute solution of univalent ions, the average number of ions in cm.^{3} at a distance between r and $r+dr$ from the free surface of the liquid is given by

$$C_r=C_\infty e^{-\frac{\epsilon^2}{2DkTa}\left(1-\frac{r}{a}\right)}dr \tag{5}$$

as it was shown in the previous paper.[1] In equation (5) $m=\frac{1}{a}=\sqrt{\frac{8\pi C_\infty\epsilon^2}{DkT}}$, where C_∞ is the average number of ions in cm.^{3} at a distance sufficiently far away from the surface, D the dielectric constant of the solution, k the Boltzmann constant, ϵ the charge of the ions.

The surface energy ΔU_s per unit area of the surface of the liquid, therefore, will be given by

$$\Delta U_s = \int_0^a C_r \frac{\epsilon^2}{2aD}\left(1-\frac{r}{a}\right)dr$$

$$= \int_0^a C_\infty \frac{\epsilon^2}{2Da}\left(1-\frac{r}{a}\right)e^{-\frac{\epsilon^2}{2DakT}\left(1-\frac{r}{a}\right)}dr. \qquad (6)$$

If we let $y=\left(1-\frac{r}{a}\right)$, $b=\frac{\epsilon^2}{2DakT}$, the above integral becomes $\frac{C_\infty \epsilon^2}{2D}\int_0^1 ye^{-by}dy$.

Since by the fundamental assumption of Debye-Hückel theory $b<1$, we can calculate the above integral and obtain

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D}\left(1-\frac{2b}{3}\right). \qquad (7)$$

Since b is small compared with 1 for very dilute solutions, we shall neglect it entirely, and write

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D}.$$

Substituting this in equation (4), we get

$$\Delta\sigma = -\frac{\epsilon^2 C_\infty}{4D} T\int_\infty^T \frac{dT}{T^2} = \frac{\epsilon^2 C_\infty}{4D}. \qquad (8)$$

If we use molar concentration c per c.c. instead of number of ions in cm.^{3} we get

$$\Delta\sigma = \frac{\epsilon^2 cN}{2D} \qquad (9)$$

where N is the Avogadro's number. This agrees except a factor 1/2 with the value found by Oka by a more elaborate yet possibly not much more rigorous calculations. The detailed comparison between the value of $\Delta\sigma/c$ found by experiments and the theoretical value of $\epsilon^2 N/2D$ was made in the previous theory of the present author[1]. There the agreement between the theory and the experiment was shown to be satisfactory.

Now according to the theory of Debye and Hückel for concentrated solutions of strong electrolyte, the potential energy of an ion due to its ion atmosphere is given by $-\frac{\epsilon^2 m}{D(1+md)}$ where d is the diameter of ions. Therefore the equation (7) is accordingly modified, and given in the first approximation by

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D(1+md)}\left(1+\frac{2b'}{3}\right), \tag{10}$$

where $$b' = -\frac{\epsilon^2}{2aDkT(1+md)}.$$

Corresponding to equation (9), we get for the increase in surface tension

$$\frac{\Delta\sigma}{c} = \frac{\epsilon^2 N}{2D(1+md)}\left(1+\frac{2b'}{3}\right). \tag{11}$$

More general case. It is easy to extend the above theory to a more general case in which kinds of ions are homogeneously distributed in the solution. Let us suppose that the charges for S kinds of ions are represented by $z_1\epsilon, z_2\epsilon, \ldots, z_i\epsilon, \ldots, z_s\epsilon$ and the concentrations (no. in cm.^{3}) by $C_1, C_2, \ldots C_i, \ldots, C_s$ respectively. The potential energy of the i th ion species due to its ion atmosphere is $-(z_i\epsilon)^2\frac{m}{D}$, where

$$m^2 = \frac{4\pi\epsilon^2}{DkT}\sum_{i=1}^{s} C_i z_i^2.$$

Therefore the increase in the surface tension is given by

$$\Delta\sigma = \frac{\epsilon^2}{4D}\sum_{i=1}^{s} C_i z_i^2.$$

Therefore if we had solutions of the same molar concentration of, for example, KCl and Na_2SO_4, the change of surface tension should be in the ratio 2 to 6. If we take 1/2 molar concentration for solutions of binary mixture of uni- and bi-valent ions, and the molar concentration for solutions of univalent ions, the ratio of change of surface tension is 6 to 4 respectively. Table 1 gives data for a few solutions of dilute concentrations taken from Heydweiller's paper. As we see in the table, the theoretical prediction is satisfied approximately in the case of K_2SO_4, $SrCl_2$, and $BaCl_2$, however, for $MgCl_2$ and Na_2SO_4 the ratio is about 4 to 4. Considering the experimental difficulty in obtaining accurate result, the agreement here obtained may be considered quite satisfactory.

(6) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.

Table 1.* Increase of Surface Tension of Strong Electrolyte.

σ: the surface tension of solution; σ_0: the surface tension of pure water;
c: the molar concentration; $\Delta = 100\ \frac{\sigma-\sigma_0}{c\sigma_0}$

NaCl		KCl		1/2 $MgCl_2$		1/2 Na_2SO_4	
c	Δ	c	Δ	c	Δ	c	Δ
0.020	2.61	0.025	2.55	0.269	2.00	0.210	2.46
0.059	2.33						
0.093	2.30	0.090	2.38	0.336	1.97	0.321	2.16
0.123	2.30	0.114	2.34	0.539	1.84	0.330	2.37
0.251	2.13						
0.290	2.11	0.225	2.26	0.808	1.74	0.428	2.16

1/2 K_2SO_4		1/2 $SrCl_2$		1/2 $BaCl_2$	
c	Δ	c	Δ	c	Δ
0.031	2.39	0.036	3.16	0.103	2.68
0.052	2.38	0.071	2.99	0.131	2.49
0.093	2.37	0.107	2.89	0.247	2.28
0.124	2.16	0.132	2 88	0.306	2.24
0.150	2.13	0.192	2.78	0.353	2.25
0.208	2.08	0.203	2.71		
0.217	2.11				

* Data taken from Heydweiller's paper, *loc. cit.*

Interfacial tension. The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydro-carbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore, the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis[7] on the interfacial tension of hydro-carbon oil against aqueous solution of metallic salt, namely, the lowering of the interfacial tension occurred by the addition of $CuCl_2$, $AgNO_3$, KCl. Since each of these substances raises the

(7) McLewis, *Phil. Mag.*, (6), **17** (1909), 466.

surface tension of water against air, and does not influence that of organic liquid, so that the interfacial tension might be expected to be raised. McLewis used a dynamical method for the measurement of interfacial tension. M. Kidokoro[8] recently repeated the experiment using both dynamical and statical method, and found that the interfacial tension is raised by the addition of inorganic salt in the water phase. The increase in the interfacial tension between normal hexane from petroleum and water by the addition of inorganic salt run parallel to that of the surface tension of the salt solution, as is expected from the theoretical anticipation. However, the magnitude of rise in the interfacial tension was about 2/3 of the rise in the surface tension of the salt solution for the same concentration.

The decrease in the rise of interfacial tension between hexane and water from that of water and air would possibly be accounted for by the consideration that there exists an electric force acting on the layer of hexane molecules due to the incomplete neutralization of the charge of any ion by the ion atmosphere of opposite charge at the vicinity of the surface. The molecules of hydro-carbon oil may orient themselves in such a way as to decrease the interfacial tension between the two phases. To attempt quantitative account for this effect will be too speculative since we have not yet any experimental evidence of molecular reorientation of hexane at the interface when inorganic salt is added.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

A very comprehensible theory of surface tension of Debye-Hückel electrolyte is proposed. An explicit formula for surface tension is derived and compared with experiment very satisfactorily. A qualitative explanation of Heydweiller effect is given. Interfacial tension is also discussed very briefly.

(8) This Bulletin, **7** (1932), 280.

A Theory of Surface Tension of Ternary Solutions.

By Kyozo ARIYAMA.

(Received June 20th, 1936.)

Since Heydweiller and his co-workers[1] discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts have been made to explain the phenomenon. The theories so far advanced may be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface energy caused by the electrostatic force of the ions. Theories of Wagner,[2] Shiba,[3] and Oneager and Samaras[4] belong to the former, while theories of Oka[5] and Ariyama[6] (present author) belong to the latter category. Aside from a great mathematical difficulty involved in the theories of the former category, the use of the theory of images in the atomic realm without justification was rather objectionable. However, until very recently there was not any experimental evidence to decide which theory is right. It seems that the experiment of Belton[7] conclusively favours the theories of latter category. The present author intends to show a reason for it in the following discussions.

The amount of ions negatively adsorbed at the surface of the solution of an aqueous salt is given by the Gibbs equation

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c}\right)={}_0\Gamma\left(\frac{1}{c}+\frac{\partial \log f}{\partial c}\right). \tag{1}$$

Where f is the activity coefficient of the salt and ${}_0\Gamma$ its negative adsorption. When a non-electrolyte is added to the system this simple relation does not apply, but becomes, when the surface concentration of one of the components is put equal to zero,

$$\begin{aligned} d\sigma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \\ &= -\Gamma_1 2RTd \log f_1C_1 - \Gamma_2 RTd \log f_2C_2, \end{aligned}$$

(1) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.
(2) Wagner, *Phys. Z.*, **25** (1924), 474.
(3) Shiba, *Bull. Inst. Phys. Chem. Research*, (Tokyo), **13** (1934), 190.
(4) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.
(5) Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(6) Ariyama, this Bulletin, **11** (1936), 687.
(7) Belton, *Trans. Faraday Soc.*, **31** (1935), 1420.

where μ_1 and μ_2 are the chemical potentials, f_1 and f_2 the activity coefficients of electrolyte and non-electrolyte respectively. Γ_1 and Γ_2 are their corresponding adsorption and C_1 and C_2 are their molal concentrations. If the concentration of the non-electrolyte is kept constant, this may be written

$$-\left(\frac{\partial\sigma_{12}}{\partial c_1}\right)_{c_2} = 2RT\Gamma_1\left[\frac{1}{c_1}+\left(\frac{\partial \log f_1}{\partial c_1}\right)_{c_2}\right]+RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \tag{2}$$

Now for dilute solution of Debye-Hückel electrolyte the surface tension was experimentally found to be given by

$$\rho-\sigma_0 = K_1C_1, \tag{3}$$

where σ_0 is the surface tention of water, K_1 a constant, C_1 the molal concentration of the salt.

If the change of activity of the salt is unaffected by the non-electrolyte,[8] (1), (2), and (3) may be combined to give

$$\left(\frac{\partial\sigma}{\partial c_1}\right)_{c_2} = K\frac{\Gamma_1}{{}_0\Gamma_1}-RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \tag{4}$$

Since $\log f_2$ is given by Debye-McAaulay,[9] it is possible to calculate $\Gamma_1/{}_0\Gamma_1$ if we determine $(\partial\sigma/\partial c_1)c_2$ experimentally. Such an experiment was carried out by Belton[10] for systems of ethyl alcohol-water salt and acetic acid-water-salt. He discovered that 2 % of ethyl-alcohol mixed in water lowers the surface tension of the solution when the concentration of salt is increased, and that acetic acid-water-salt system increases the surface tension of the solution as the concentration of salt is increased. The calculated values of Γ_1/Γ_0 showed values always less than one for salts like KBr, K_2SO_4, $KClO_2$, and KNO_3. For NH_4Cl the value was about 1.2 for dilute concentration.

These results are difficult to be accounted for by the theories of surface tension based on the theory of images, but are easily accounted for by the theories of Oka[5] and Ariyama.[6]

It is well known that non-electrolyte are positively adsorbed at the free surface of the solution. Therefore let us assume, for simplicity of discussion, that the adsorption layer has thickness d, and the dielectric constant of this layer is D'_a. The dielectric constant of electrolyte solution is represented by D, and the dielectric constant of mixture of electrolyte and non-electrolyte solution sufficiently far away from the surface is represented by D'.

(8) Theoretical proof of this assumption will be given in this Bulletin shortly by the present author.

(9) Debye and McAaulay, *Physik. Z.*, **26** (1925), 22.

(10) See (7).

Then the repulsive force acting on the ions of charge $+\epsilon$ at a distance r from the surface of the electrolyte solution is given by $j\epsilon^2/4r^2D$ if we assume the image force at the boundary of water and air. In the above expression $j = D-1/D+1$. If non-electrolyte like ethyl-alcohol, which has much smaller dielectric constant than water, is added, D' will be in general smaller than D. The repulsive force for the ion in the mixture becomes $j'\epsilon^2/4r^2D'$. Now $j' = D'-1/D'+1$ will be smaller than j but D' in the denominator becomes smaller in the same order, the repulsive force outside of the adsorption layer remains almost unchanged. This can be seen very clearly if we take a specific example, and calculate each quantity specifically. Now in the adsorption layer D'_a will be very small compared with D for alcohol. Therefore $j'_a\epsilon^2/4r^2D'_a$ becomes larger than $j\epsilon^2/4r_2D$ since increase in $1/D'_a$ outweighs the decrease in j'_a. Therefore it is apparent that the addition of non-electrolyte tends to increase the negative adsorption of ions: or in any case will not decrease the negative adsorption except for those substances which have higher dielectric constants than water. This entirely contradicts the experimental fact that $\Gamma_1/{}_0\Gamma_1$ is much smaller than unity. Therefore the theory of surface tension based on 'image force' seems incompatible with the experimental data.

Next let us consider the question of how Oka's theory will be applied in this case. Let us consider an ion of charge $+\epsilon$ situated at a distance x from the surface. We shall take a cylindrical coordinate origin at this point, choosing z axis normal to the surface. Then for $x < d$, the dielectric constant is D'_a, and for $x > d$, the dielectric constant is D'. For simplicity of notation let us write these as $D'_a = D$, and $D' = D_2$. The surface of the solution is taken as $x = 0$. We set up Debye-Hückel equations

$$\begin{aligned} \Delta\psi_1 &= k_1^2\psi_1 \\ \Delta\psi_2 &= k_2^2\psi_2 \\ \Delta\psi' &= 0\,, \end{aligned} \tag{5}$$

where ψ_1 is a potential at (r, z) in the adsorption layer d, ψ_2 is a potential at (r, z) in the bulk of the solution, and ψ' is the potential at any point in the air. k_1 and k_2 are given by

$$k_1^2 = \frac{8\pi n\epsilon^2}{D_1kT}, \quad k_2^2 = \frac{8\pi n\epsilon^2}{D_2kT},$$

where n is the average number of ions in c.c.

We want to determine ψ_1 and ψ_2 under the following boundary conditions

$$\psi_{1z=x} = \psi'_{z=x}$$

$$D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x} = \left(\frac{\partial\psi'}{\partial z}\right)_{z=x}$$

$$\psi_{1z=x_1'-x-d} = \psi_{2z=x_1} \tag{6}$$

$$D_2\left(\frac{\partial\psi_2}{\partial z}\right)_{z=x_1} = D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x_1} .$$

Suppose we obtained solutions for ψ_1 and ψ_2 satisfying these conditions. Then the negative adsorption is given by

$$\Gamma = -n\int_0^d\left(1-e^{-\frac{\varphi_1(x)}{kT}}\right)dx - n\int_d^\infty\left(1-e^{-\frac{\varphi_2(x)}{kT}}\right)dx \quad . \tag{7}$$

where $\varphi_1(x) = \varphi_{1+}(x) = \varphi_{1-}(x) = \epsilon\psi_{1+} = -\epsilon\psi_{1-}$

and $\varphi_2(x) = \varphi_{2+}(x) = \varphi_{2-}(x) = +\epsilon\psi_{2+}(x) - \epsilon\psi_{5+}(\infty)$

$$= -\epsilon\psi_{2-}(x) + \epsilon\psi_{2-}(\infty)$$

So let $\varphi_2 = \psi(x) - \psi(\infty)$

If we write eq. (5) in full, we get

$$\frac{\partial^2\psi_1}{\partial r^2} + \frac{1}{r}\frac{\partial\psi_1}{\partial r} + \frac{\partial^2\psi_1}{\partial z^2} = k_1^2\psi_1, \text{ etc.}$$

We shall let the solutions take the following from

$$\psi_1 = \int_0^\infty\left[A(\alpha)e^{\sqrt{\alpha^2+k_1^2}z} + B(\alpha)e^{-\alpha z}\right]J_0(\alpha r)d\alpha$$

$$\psi_2 = \int_0^\infty\left[D(\alpha)e^{\sqrt{\alpha^2+h_2^2}z} + \frac{\alpha}{D_1\sqrt{\alpha^3+k_2^2}}e^{-\sqrt{\alpha^2+k_2^2}z}\right]\delta_0(\alpha r)dr$$

$$\psi' = \int_0^\infty C(\alpha)e^{-\alpha z}J_0(\alpha r)d\alpha,$$

where $A(\alpha)$, $B(\alpha)$, $C(\alpha)$, and $D(\alpha)$ are the coefficients that have to be determined by 4 boundary conditions. $J_0(\alpha r)$ is the Bessel functions of zero order.

It is easy to obtain these coefficients, and they are given by

$$A(\alpha) = \frac{-2\alpha(1-D_1\alpha)e^{-\alpha x-\sqrt{\alpha^2+k_2^2}x_1}}{P}$$

$$B(\alpha) = \frac{+2\alpha(\alpha+D_1\sqrt{\alpha^2+k_1^2})e^{\sqrt{\alpha^2+k_1^2}x-\sqrt{\alpha^2+k_2^2}x_1}}{P},$$

where $$P = (\alpha-D_1\sqrt{\alpha^2+k_1^2})(D_2\sqrt{\alpha^2+k_2^2}+D_1)e^{\sqrt{\alpha^2+k_2^2}x-\alpha_1}$$

$$-(D_1\sqrt{\alpha^2+k_1^2}-D_2\sqrt{\alpha^2+k_2^2})(1-D_1\alpha)e^{\sqrt{\alpha^2+k_1^2}x_1-\alpha x}$$

and $C(\alpha)$ and $D(\alpha)$ are obtained from the following boundary equations:

$$A(\alpha)e^{\sqrt{\alpha^2+k_1^2}x}+B(\alpha)e^{-\alpha x} = C(\alpha)e^{-\alpha x}$$

and $$A(\alpha)e^{\sqrt{\alpha^2+k_1^2}x_1}+B(\alpha)e^{-\alpha x_1} = D(\alpha)e^{\sqrt{\alpha^2+k_2^2}x_1}+\frac{\alpha}{D_2\sqrt{\alpha^2+k_2^2}}e^{\sqrt{\alpha^2+k_2^2}x_1}.$$

Thus[11] $$\varphi_1(x)/\epsilon^2 = \int_0^\infty A(\alpha)d\alpha+\int_0^\infty B(\alpha)d\alpha \qquad (8)$$

and $$\varphi_2(x)/\epsilon^2 = \int_0^\infty D(\alpha)d\alpha.$$

Therefore the formal solution of the problem is obtained. But since expressions for $\varphi_1(x)$ and $\varphi_2(x)$ are so complicated, that it is not possible to evaluate the negative adsorption I' unless some method of simplification is discovered. However, it may be possible that this sort of theory might reproduce a result which is demanded by the experimental fact that $I'_1/{}_0I'_1$ is smaller than unity.

Now we shall discuss the application of the theory[6] that the present author has proposed recently. If we consider an adsorption layer of thickness d at the surface, the potential energy of inward force for ions is accordingly modified. Let the dielectric constant in d be D' and the dielectric constant of the bulk of the solution be D. The thickness of the ion atmosphere in d be represented by a', and in the solution by a. Then in the first approximation, the potential energy of inward force on an ion situated at a distance $r(a+d)$ from the surface is given by

$$E = \frac{\epsilon^2}{2Da}\left[1-\left(\frac{r-d}{a}\right)\right]-\frac{\epsilon^2}{2D'a'}\left[1-\frac{(r-d)}{a'}\right]+\frac{\epsilon^2}{2D'a'}\left(1-\frac{r}{a'}\right)$$

$$= \frac{\epsilon^2}{2Da}\left(1-\frac{r}{a}\right)+\frac{\epsilon^2}{2Da}\left(\frac{d}{a}\right)-\frac{\epsilon^2}{2D'a'}\left(\frac{d}{a'}\right).$$

(11) See Oka's paper in this connection.

According to the Maxwell-Boltzmann statistics, the probability that an ion lies at a distance r and $r+dr$ will be proportional to $e^{-\frac{E}{kT}}dr$. Therefore if C is the average number of ions in cm.^{3} the number of ions at a distance between r and $r+dr$ will be given by

$$C_r = Ce^{-\frac{E}{kT}}dr.$$

Therefore the negative adsorption is given by

$$\Gamma = -C\int_0^{a+d}\left(1-e^{-\frac{E}{kT}}\right)dr.$$

Substituting the value of E in the above equation, and carrying out the integration, we obtain after simplification

$$\Gamma = -\frac{c}{kT}\left[\frac{\epsilon^2}{4D}+\frac{\epsilon^2}{4D}\left(\frac{d^2+2da}{a}\right)-\frac{\epsilon^2}{2D'}-\left(\frac{da+d^2}{a'^2}\right)\right]. \qquad (9)$$

The first term represents the amount of adsorption which would result if the adsorption layer d of dielectric constant D' were not present. Since in general $D > D'$ and $a > a'$, the third term is much larger than the second term. In other words the negative adsorption decreases as the adsorption layer d increases.

Since for mixture of alcohol-water-salt solutions in Belton's experiment the dielectric constant of the system is not appreciably different from that of aqueous solutions, the decrease in negative adsorption must be attributed to the effect we have discussed above.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

The theories of surface tension of Debye-Hückel electrolyte can be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface free energy caused by the electrostatic force of ions. On the basis of experimental evidence on the surface tension of ternary solution, the theories of former category are shown to be unacceptable. Theories of Oka and also of Ariyama which belong to the latter category are applied to explain the surface tension of ternary solutions. Agreement with experiment is satisfactory.

A Note on the Osmotic Coefficient and the Activity Coefficient at the Surface.

By Kyozo ARIYAMA.

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The exact theoretical calculation of the negative adsorption of Debye-Hückel electrolyte requires the knowledge of activity coefficient of the solute at the surface of the solution. The surface tension of the solution is given by the Gibbs thermodynamic equation.

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c}\right)=\,_0\Gamma\left(\frac{1}{c}+\frac{\partial\log f}{\partial c}\right), \tag{1}$$

where σ is the surface tension of the solution, c the molar concentration of solute, Γ the negative adsorption, f the activity coefficient of the solute at the surface of the solution. If a non-electrolyte is added to the system, the above simple equation does not apply, but become if the concentration of non-electrolyte is kept constant.

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c_1}\right)_{c_2}=2RT\Gamma_1\left[\frac{1}{c_1}+\left(\frac{\partial\log f_1}{\partial c_1}\right)_{c_2}\right]+RT\Gamma_2\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}. \tag{2}$$

Now for dilute solution of Debye-Hückel electrolyte, the surface tension is experimentally found to be given by

$$\sigma-\sigma_0=KC_1, \tag{3}$$

where σ_0 is the surface tension of water, K a constant.

In order to calculate the change of negative adsorption due to the addition of non-electrolyte, Belton[1] assumed the relation $\frac{\partial\log f}{\partial c}=\left(\frac{\partial\log f_1}{\partial c_1}\right)_{c_2}$ at the surface and $\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}$ is the same at the surface of the solution as in the interior of the solution.

Then by equations (1), (2), and (3) we get

$$\left(\frac{\partial\sigma_{12}}{\partial c_1}\right)_{c_2}=K_1\frac{\Gamma_1}{{}_0\Gamma_1}-RT\Gamma_2\left(\frac{\partial\log f_2}{\partial c_1}\right)_{c_2}. \tag{4}$$

(1) Belton, *Trans. Faraday Soc.*, **31** (1935), 1420.

Therefore we can calculate the value of $\Gamma_1/{}_0\Gamma_1$ knowing all the other factors in the equation. The present author wishes to prove theoretically by taking a specific example that the above two assumptions that Belton made is justified.

Osmotic coefficient of ions at the surface.(2) We shall first consider the total mutual potential energy of the ions with respect to their ionic atmospheres, considering mono-mono-valent electrolyte first for the sake of simplicity. The potetial energy of one ion of charge $+\epsilon$ as well as $-\epsilon$ is equal to $-\frac{\epsilon^2 m}{D}$, where $m^2 = \frac{8\pi C_\infty \epsilon^2}{DkT}$, D is dielectric constant of the solution, C_∞, the average number of ions in cm.^{3} If we have altogether $2N$ ions, the total potential energy is therefore $-\frac{N\epsilon^2 m}{D}$ since if we have a number of charges e_i at points where the potentials are ψ_i, the total potential energy is given by

$$U = \frac{1}{2}\sum e_i \psi_i .$$

As is shown in the previous paper, the potential energy of an ion near the surface is greater than the potential energy of an ion sufficiently far away from the surface. The ion which is situated at a distance $r < \frac{1}{m}$ from the surface of the solution has potential energy $-\frac{\epsilon^2 m}{2Da}\left(1-\frac{r}{a}\right)$, where $a = 1/m$. Since N is the average concentration of the positive ions in the solution, the total lack of potential energy for the unit surface of depth a is given by

$$\Delta U = \frac{\epsilon^2 N}{4D}.$$

Therefore the average total potential energy per cm^3 at the surface is given by

$$U = -\left(\frac{N\epsilon^2}{aD} - \frac{N\epsilon^2}{4Da}\right) = -\frac{3}{4}\frac{N\epsilon^2}{aD}.$$

This result can easily be generalized for an electrolyte containing $N_1, \ldots, N_i, \ldots, N_s$ ions of valencies $z_1, \ldots, z_i, \ldots, z_s$. In this case the potential energy of the central ion with respect to its ionic atmosphere is given by $\frac{z_i^2 \epsilon^2 m}{D}$ and the potential energy of the solution is then given by

$$U_e = -\sum_i \frac{3}{8}\frac{N_i z_i^2 \epsilon^2 m}{D}, \quad \text{where} \quad m^2 = \frac{4\pi\epsilon^2}{DkT}\sum_i N_i z_i^2 .$$

(2) The argument presented in the following follows closely the Debye's theory presented by Falkenhagen in "Electrolyte."

The total electric work w necessary to discharge and recharge the ions at the surface becomes correspondingly

$$W = -\sum \frac{1}{3}\frac{3}{4}\frac{N_i\epsilon^2 z_i^2 m}{D}$$

$$= -\sum \frac{1}{4}\frac{N_i\epsilon^2 z_i^2 m}{D}.$$

In order to calculate the osmotic pressure, we must differentiate the electrical work with respect to the volume V. It must be noted that the expression for m contains V implicitly since $n_i = N_i/V$, $e_i = \epsilon z_i$ we have $\frac{\partial w}{\partial V} = \frac{\partial w}{\partial m}\cdot\frac{\partial m}{\partial V} = -\sum \frac{N_i e_i^2}{4D}\cdot\frac{\partial m}{\partial V}$ since $\frac{\partial m}{\partial V} = -\frac{m}{2V}$, we get

$$\frac{\partial W}{\partial V} = \sum \frac{n_i e_i^2 m}{8D}.$$

The osmotic pressure of real solution is given by

$$P = \sum n_i kT - \sum \frac{n_i e_i^2 m}{8D}$$

$$= \sum\left(1-\frac{e_i^2}{8DkT}\right)n_i kT = \sum g_i n_i kT, \qquad (5)$$

where $g_i = 1-\frac{e_i^2}{8DkT}$ is called osmotic coefficient of the ions. The osmotic coefficient of the ions in the interior of the solution is given by

$$G_i = 1-\frac{e_i^2}{6DkT}.$$

We see that the osmotic coefficient of the ions is slightly greater at the surface than in the interior of the solution.

Activity coefficient of ions at the surface. With the parallel argument with that of Debye, the thermodynamic potential of the real solution Φ is given by

$$\Phi = \sum_0^s N_i\left(\Phi_i + kT\log y_i - \frac{e_i^2 m}{4D}\right),$$

where Φ_i's depend only on the pressure and temperature, and y_i is the mol fraction of the solute.

The change of thermodynamic potential with changing temperature and pressure being kept constant is given by

$$\delta\Phi = \sum_{i=0}^{s} \delta N_i \left[\Phi_i + k \log y_i - \frac{e_i^2 m}{4D} - \sum_{j=0}^{s} \frac{e_i^2}{4D} N_i \frac{\partial m}{\partial N_i} \right].$$

If the index i refers to the dissolved particles, i.e., one of the values $i = 1, 2, \ldots, s$ we have

$$\sum_{j=0}^{s} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_i} = \frac{e_i^2 m}{8D} \quad \text{for} \quad i = 1, \ldots, s .$$

If on the other hand, $i = 0$ i.e. we are dealing with variations in the solvent, we may proceed as follows. We can write the total volume of the solution V in the linear form

$$V = V_0 N_0 + \sum^{s} N_i v_i ,$$

where v_0 and v_i represent the changes in the total volume caused by adding respectively a molecule of the solvent or a particle of the sort the solution. We then have

$$\frac{\partial m}{\partial N_i} = \frac{\partial m}{\partial V} \frac{\partial V}{\partial N_0} = V_0 \frac{\partial m}{\partial V} = -\frac{V_0}{2V} m$$

and hence

$$\sum_{j} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_0} = -V_0 \frac{n_j e_i^2}{8D} .$$

The total variation in thermodynamic potential is thus

$$\delta\Phi = \delta N_0 \left[\Phi_0 + kT \log y_0 + v_0 \sum \frac{n_j e_j^2 m}{8D} \right]$$

$$+ \sum_{1} \delta N_i \left[\Phi_i + kT \log y_i - \frac{3}{8} \frac{e_i^2 m}{D} \right].$$

The coefficient of δN_i is termed the chemical potential. In the case of ideal dilute solution, the chemical potential is given by

$$\xi_i = \Phi_i + kT \log y_i$$

The chemical potential of the real solution is obtained by replacing the concentration y_i by the activity $f_i y_i$ for dilute solutions, where f_i being the activity coefficient. We then have

$$\xi_i = \Phi_i + kT \log (f_i y_i).$$

Thus $$\log f_i = -\frac{3}{8} \frac{e_i^2 m}{DkT}. \tag{6}$$

The activity of the solvent is also affected by the dissolved ions, the activity coefficient being given by

$$\log f_0 = v_0 \sum_j \frac{n_j e_j^2 m}{8DkT}. \tag{7}$$

Thus the decrease in the activity coefficient of the ions at the surface is smaller than that of the interior. The increase in the activity coefficient of the solvent at the surface is also smaller than that of the interior.

The limiting law for the activity coefficients of binary salts in water at the surface is given by

$$0°\text{C.} \quad \log f = -0.839\sqrt{J},$$

$$15°\text{C.} \quad \log f = -0.860\sqrt{J},$$

$$20°\text{C.} \quad \log f = -0.872\sqrt{J},$$

where J is the ionic strength defined by

$$J = \frac{1}{2} \sum \gamma_i z_i^2$$

and γ_i is expressed in moles per litre.

Thus we get for

$$\frac{\partial \log f}{\partial J} = -0.419 \frac{1}{\sqrt{J}}.$$

Therefore for concentration $J = 0.01$, the absolute magnitude of $\frac{d \log f}{dJ}$ is about 4.2 % of the value of $\frac{1}{J}$. Therefore for very dilute solutions this term can be neglected in rough calculations.

Osmotic pressure and activities in dilute mixture of electrolyte and non-electrolyte. In order to find the additional free energy caused by the pressence of the ionic charges, we shall proceed in the same way as before. We imagine the ions discharged in an infinitely dilute solution, and recharged in a solution of finite concentration. If the solution contains $N_1, \ldots, N_i, \ldots,$

N_s ions of the species $1, \ldots, i, \ldots, s$ having charges $e_1, \ldots, e_i, \ldots, e_s$ the work necessary to carry out this process W is given by

$$W = -\sum \frac{N_i e_i^2}{2D_0 b_i} + \sum \frac{N_i e_i^2}{2D_m b_i} - \sum \frac{N_i e_i^2 m}{4D_m}. \tag{8}$$

For the sake of simplicity, an ion of the i th sort is considered as a sphere of radius b_i which is charged in pure water of dielectric constant D_0, and subsequently in the solution of given concentration D_m at the surface of the solution. m is the reciprocal thickness of the ionic atmosphere. Since we are dealing only with a first approximation, we can represent the dielectric constant of the mixture D_m by the linear interpolation formula.

$$D_m = D_0(1-\alpha n-\beta n'), \tag{9}$$

where n and n' represent the number of molecules of non-electrolyte and electrolyte respectively per c.c., and α and β are two constants which may be determined from experiment.

We introduce (9) in (8) and expand $1/D_m$ in the 2nd term in powers of n and n', retaining only the 1st term of the expansion, and write D_0 for D_m in the third term. We then have

$$W = \alpha n \sum \frac{N_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{N_i e_i^2}{2D_0 b_i} - \sum \frac{N_i e_i^2 m}{4D_0}.$$

Thus we get

$$-\frac{\partial W}{\partial V} = \alpha n \sum \frac{n_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{n_i e_i^2}{2b_i D_0} - \sum \frac{n_i e_i^2 m}{8D_0},$$

where $n = N/V$, $n' = N'/V$.

If one molecule of the electrolyte dissociate into ν_i of the species $1, \ldots, \nu_s$ of the species s, having valencies $z_1, \ldots, z_i \ldots, z_s$, we have $n_i = \nu_i n'$, $e_i = z_i \epsilon$. Introducing abreviations

$$\nu = \sum \nu_i$$

$$P_N = nkT$$

$$P_E = \nu n' kT\left(1 - \frac{n_0 \epsilon^2}{8D_0 kT} \frac{\sum \nu_i z_i^2}{\nu}\right)$$

$$p = \alpha \frac{n \nu n' \epsilon^2}{2D_0 \nu} \sum \frac{\nu_i z_i^2}{b_i}$$

we can write for the osmotic pressure

$$P = P_N + P_E + p. \tag{10}$$

Thus the effect of surface on the osmotic pressure appears only in osmotic pressure P_E which would be exerted by the $n'\nu$ ions of electrolyte if present alone in the surface phase.

The effect of surface is to increase the osmotic pressure P_E slightly.

We shall now calculate the effect of the electrolyte on the activity of the non-electrolyte at the surface of the solution. If we write the electrical energy contribution W in the form $W = \Sigma N_i \bar{\omega}_i$, where $\bar{\omega}_i = \omega_i / N$ the activity potential h_i is defined by

$$\log h_i = \frac{\bar{\omega}_i}{kT} = \frac{\alpha n e_i^2}{2D_0 b_i kT} + \beta \frac{n' e_i^2}{2D_0 b_i kT} - \frac{e_i^2 m}{4D_0 kT}.$$

The activity potential of the non-electrolyte is unity, and only the activity potential of the ions differs from unity. Activity coefficient f_i of any component i is

$$\log f_i = \log h_i + \sum_j N_j \frac{\partial \log h_i}{\partial N_i}.$$

Since $h = 1$, $\log h = 0$. Activity coefficient of non-electrolyte is given by

$$\log f = \alpha \sum \frac{n_j e_j^2}{2D_0 b_i kT}. \tag{11}$$

Thus the activity coefficient of non-electrolyte at the surface of the solution is the same as the activity coefficient in the bulk of the solution in the first approximation.

The activity coefficient of ions at the surface is calculated by means of

$$\sum_j N_j \frac{\partial \log h_i}{\partial N_i} = -\frac{1}{8} \frac{e_i^2 m}{D_0 kT}.$$

The second term of $\log h_i$ can be neglected for solution of dilute concentration. Then

$$\log f_i = \frac{\alpha n e_i^2}{2D_0 b_i kT} - \frac{3}{8} \frac{e_i^2 m}{D_0 kT}. \tag{12}$$

Since n is the concentration of non-electrolyte,

$$\left(\frac{\partial \log f_i}{\partial c_1}\right)_{c_2} = \frac{\partial \log f_i}{\partial c_1}.$$

This is what we wanted to prove. From the above discussion it may be apparent that the above relation will hold for the case in which a more general form of energy is assumed than the one discussed in the paper.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

The osmotic pressures and the activity coefficients for strong electrolyte solution and for solutions of mixture of electrolyte and non-electrolyte at the surface are calculated on the basis of Debye-Hückel theory. Some relations between the activity coefficients for two cases are given.

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The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. IV. The Effect of the Ferro-magnetic Metals Free from Oxides. Remarks on the Catalytic Action of the Ferro-magnetic Metals and Oxygen.

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The authors have found that the ferro-magnetic metals in such forms as reduced iron and reduced nickel influence the addition of hydrogen bromide to allyl bromide in the same way as oxygen and peroxides :[1] In the presence of reduced iron or reduced nickel, hydrogen bromide adds rapidly to allyl bromide (in the dark at room temperature in the absence of solvents, oxygen, and peroxides) and the greater part of the product is the abnormal addition product 1,3-dibromopropane, while in the absence of foreign substances the addition is slow and proceeds mainly to the formation of the normal product 1,2-dibromopropane. A difference, however, exists between these two groups of catalysts in that, while the influence of oxygen or peroxides is totally eliminated by

(1) The first paper of this series, this Bulletin, **11** (1936), 692.

the addition of an antioxidant such as diphenylamine, the effect of the ferro-magnetic metals undergoes no modification in the presence of the antioxidant.[2] Now, with a special precaution of removing traces of oxides from the reduced metals, the ferro-magnetic metals have been found more effective in the sense of the predomination of 1,3-dibromopropane in the product of addition of hydrogen bromide to allyl bromide than in the previous experiments carried out with no such precaution.

In the previous experiments with freshly reduced nickel the percentage of 1,3-dibromopropane in the addition product was found 68[1], 63[1], and 58[2]. Reduced nickel used in those additions was prepared under the conditions suitable for the preparation of the hydrogenating catalyst by passing pure hydrogen gas over nickel oxide (Kahlbaum, "cobalt free") heated at 300–400°. Reduction might possibly be incomplete at this temperature, and, moreover, the metal reduced in this way evolved heat when taken to the air. Thus it may be suspected that even freshly reduced nickel was not free from traces of oxides.[3] As it was really found that the power of accelerating the abnormal addition is far diminished by keeping reduced nickel long in the air,[2] it seemed very important to examine the effect of reduced nickel free from oxides. For this purpose nickel oxide was reduced at a higher temperature (dull red-heat). The metal was obtained in a loosely coalescent form crumbling readily on shaking and evolved heat when taken to the air. The metal (3.5 g.) contained in the reaction tube was again heated at 300–400° in the atmosphere of hydrogen, then, without entrance of air, treated in vacuum at 250°, and washed with hydrogen bromide gas. Hydrogen bromide (20 g.) and allyl bromide (24 g.) collected in the mixing tube were then distilled in vacuum into the reaction tube containing reduced nickel. The reaction tube was sealed off without entrance of air, slipped into an iron pipe, and shaken at room temperature for three days. The contents were treated as described previously.[4] The results are shown in the accompanying table (exp. 1 and exp. 2). Ninety-five per cent. of the product was 1,3-dibromopropane in both experiments. The reduced nickel appeared to have not suffered the slightest attack by hydrogen bromide and the liquid remained colourless after reaction.

In the additions in the presence of commercial reduced iron (Kahlbaum) about seventy per cent. of the product was 1,3-dibromopropane (see the tables of the first and the second papers).[1][2] It was already anticipated that the effect of freshly reduced iron would be more conspicuous.[5] A result as

(2) The second paper of this series, this Bulletin, **11** (1936), 754.
(3) Adsorbed or absorbed oxygen, if any, was removed by evacuating at 250° and washing with hydrogen bromide gas.
(4) For the details of the experimental procedure see the first paper.
(5) This Bulletin, **11** (1936), 756.

No. of exp.	Catalyst	Product: Dibromopropanes			
		Yield (%)	Boiling point (°C./mm.)	1,3-(%)	1,2-(%)
1	Reduced nickel free from oxides, 3.5 g.	40	44–53/11	95	5
2	Reduced nickel free from oxides, 3.5 g.	60(6)	43–54/10	95	5
3	Freshly reduced iron, 3.4 g.	40	40–53/10	92	8
4	Reduced cobalt free from oxides, 3.5 g.	30	32–46/10	38	62

shown in the table (exp. 3) has really been obtained with reduced iron prepared by freshly heating the commercial product at 300–400° in the stream of hydrogen. Reduced iron prepared in this way evolved no heat in the air. The addition was carried out in the same way as with reduced nickel, except that in this case the metal was used without treating with hydrogen in the reaction tube. The addition product was found to contain more than 90 per cent. 1,3-dibromopropane. The metal was not attacked by hydrogen bromide also in this case and the liquid remained colourless after the reaction.

On account of the fact that cobalt does not resist against the action of hydrogen bromide in allyl bromide in contrast with nickel and iron, with commercial reduced cobalt no effect, and even with freshly reduced cobalt only a small effect, on the direction of addition of hydrogen bromide to allyl bromide were observed (see the table of the second paper).[2] With reduced cobalt prepared by heating the commercial product at dull red-heat in the stream of hydrogen and freed from traces of oxides by reducing again in the reaction tube, a similar result has been obtained (exp. 4). The metal suffered seriously the attack by hydrogen bromide.

The alternating resistance of the three metals of the iron group to hydrogen bromide in allyl bromide finds its counterpart, for instance, in the alternating ease with which they form metal-carbonyls.

The results obtained with the special precaution of eliminating traces of oxides have thus established the well-defined influence of the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. They not only inverse the proportion of the normal and the abnormal addition products, but also increase the total yield of the products. Thus the effect of the ferro-

(6) The cause of the exceptionally good yield of exp. 2 is unknown, except that reduced nickel used in this experiment was prepared with nickel oxide from a new bottle (Kahlbaum, "cobalt free").

magnetic metals resembles the so-called peroxide effect of oxygen so far as the results of addition of hydrogen bromide to allyl bromide are concerned. It has now been made very probable that the peroxide effect of oxygen, and also even of peroxides, may be attributed to the action of oxygen itself and not of any formed peroxide.[7] Then, oxygen, the gaseous substance with the greatest magnetic susceptibility, and the ferro-magnetic metals exert similar influences on the addition of hydrogen bromide to allyl bromide. It may be assumed that these substances with great magnetic susceptibilities activate allyl bromide by changing the state of its molecule from a type suitable for the normal addition into one suitable for the abnormal addition, say by means of electron displacement, while platinum black with no significant influence on the composition, but with an increasing effect on the yield, of the product[8] seems to activate hydrogen bromide.

It is thinkable that in organic chemistry there may be not a few cases of the catalytic action by aerial oxygen which have hitherto been unnoticed. For instance, M.S. Kharasch and M. Foy[9] state that the presence of peroxides is necessary for the Cannizzaro reaction to take place, air or oxygen being also effective because of the formation of peroxides, and the heavy metal ions, which were once considered to accelerate the Cannizzaro reaction by themselves, have only a catalytic effect on the peroxide formation but no direct influence on the Cannizzaro reaction itself. But it may be more reasonable to consider that the heavy metal ions would facilitate the decomposition of peroxides, and that peroxides could not stay long in alkali so strong as used in the Cannizzaro reaction, unless very minute traces of peroxides are concerned. Thus it is possible that the active catalyst is really molecular oxygen. The decision awaits for further experimental evidence.

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(7) The third paper of this series, this Bulletin, **11** (1936), 798. P.L. Harris and J.C. Smith, *J. Chem. Soc.*, **1935**, 1572; "emphasize that in the absence of air the catalysts perbenzoic acid, benzoyl peroxide, 10,11-epoxyundecoic acid, and α-heptenylheptaldehyde have a very small influence on the composition of the product from hydrogen bromide and undecenoic acid," and point out that "at least with this olefin molecular oxygen is essential for the peroxide effect." But, that the peroxide effect is to be attributed to the catalytic action of molecular oxygen itself, neither is shown by their investigations, nor seems to be meant by their statement, because they summarize their results by saying "none of the catalysts is effective in absence of molecular oxygen," thus recognizing the necessity for the presence of molecular oxygen only in order that their "catalysts" may bring about the peroxide effect.

(8) See the table of the first paper, this Bulletin, **11** (1936), 693.

(9) *J. Am. Chem. Soc.*, **57** (1935), 1510.